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Testing of Hydrocarbon Emissions from Vegetation, Leaf Litter and Aquatic Surfaces, and Development of a Methodology for Compiling Biogenic Emission Inventories

Washington State Univ., Pullman

Prepared for

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16. ABSTRACT

This report outlines a general methodology for estimating emission rates of volatile organic compounds (VOC) from vegetation, soil/leaf litter, and surfaces of bodies of water. Techniques are prescribed for sample collection and analysis as well as for extrapolating the emission rates determined to estimate biogenic VOC emissions over any area. Emission factors are presented for broad classes of vegetation and for the major biotic regions in the conterminous U.S. Emission inventory procedures are illustrated by using emission factors to develop an example annual VOC emission inventory for the U.S. This nationwide emission inventory indicates that most biogenic VOC emissions can be expected during the summer months. In general, vegetation emits much larger quantities of VOC than does either leaf litter or water surfaces. Isoprene and various terpenes comprise the bulk of all vegetation emissions.

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Final Report

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by

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Prepared for

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INTRODUCTION

The regional nature of photochemical oxidant pollutant episodes has been well documented in the last few years. High oxidant (especially ozone) levels have been measured in rural areas well away from significant anthropogenic emission sources. While evidence has accumulated which indicates that oxidant precursors generated in urban centers can be transported into these rural regions, it has also been shown in smog chamber tests that biogenic volatile organic compounds (VOC) are photochemically reactive and can participate in ozone formation.

In order to define the contribution of vegetation, leaf litter, and water surfaces to the overall atmospheric burden of VOC in a specific region, an estimate of biogenic VOC emissions is essential. To this end, Washington State University, under contract to EPA, has developed testing procedures to measure emissions from vegetation, leaf litter and surface waters. As part of this effort, measurements have been made on selected plant species in North Carolina, California and Washington. Some selected results of a research project conducted by WSU in Florida funded by EPA Region IV (Contract #68-01-4432) have also been included. The results of all of these studies have been used to construct an "order of magnitude" nationwide inventory of biogenic organic emissions.

This report is designed to serve several purposes. First, it describes in detail, the equipment and methodology required to measure the

organic compound (VOC) emissions from vegetation, leaf litter and surface water. Second, it presents emission factors for vegetative species, leaf litter and the surfaces of bays, rivers and marshes that were tested during the course of this program. Third, an example nationwide annual inventory of biogenic organic emissions has been prepared.

The reader has several options available to him if he desires to compile an inventory for a particular geographical area and a particular time period. If sufficient resources are available, field measurements should be performed using the techniques described herein, and an inventory compiled by applying the resulting emission factors to the actual vegetation mix in the area of concern. In this case, the actual vegetative species distribution may be known in sufficient detail from existing information or it may have to be compiled in a separate effort. On the other hand, if few resources are available extrapolations can be made from the inventory data given herein as a coarse approximation of local organic emissions.

A detailed biogenic emission inventory for the Tampa/St. Petersburg area was compiled for Region IV EPA concurrent with this study. Summary emission rate data from the Tampa/St. Petersburg study area are included in this report. The detailed biogenic emission inventory for the Tampa/St. Petersburg area is included in the final report for EPA Contract No. 68-01-4432.

For those concerned with the development and validity of the methodology, documentation is included in an appendix explaining the evaluation and rationale of the experimental approaches considered for conducting emission tests.

1. FIELD TESTING FOR EMISSION FACTORS

There are two basic components needed for the compilation of an inventory of organic emissions from vegetation, leaf litter and water surfaces: 1) emission factors which relate organic emissions to some biological indicator (such as dry leaf biomass or surface area) over time, and 2) biomass density factors, which are measures of how much of the particular biological indicator is present in a given area. The term "biomass" as used in this report, refers to the oven dried weight of the vegetation of interest. Emission rates for vegetation were calculated in terms of leaf biomass. Emission rates for the surfaces of water and soil/leaf litter were calculated directly on the basis of the area of the surface that was sampled.

Five major steps are necessary to develop a detailed area-wide inventory.

1. Identify the major vegetation types and predominant plant species.
2. Select the representative species to be sampled.
3. Conduct a field program to collect and analyze emission samples from each of the representative species.
4. Quantify the biomass density of the major species in the inventory area.
5. Develop emission rate algorithims for the major daily and seasonal emission variables (light, temperature, moisture), that affect biogenic emissions.

This section deals with the third activity - the actual collection and analysis of field data for emission factor development. This section is broken into two major segments: 1) sampling equipment and procedures, and 2) analytical equipment and procedures.

1.1. SAMPLING EQUIPMENT AND PROCEDURES

The method developed to measure VOC emissions from vegetation combines the advantages of a static enclosure system and dynamic flow system. The system developed by WSU to sample vegetation emissions is shown in Figure 1.1-a. Basically, the method involves (1) enclosing a portion of the vegetation, (2) collecting a background sample of the enclosed air, (3) filling the enclosure bag with pure hydrocarbon free air, and (4) collecting a sample of the air in the enclosure. The samples are returned to the laboratory, the branch is clipped, and the leaves or needles within the enclosure are removed and dried. VOC emissions are equal to the difference between the mass of VOC in the bag at the time of the background sample and the mass of VOC in the bag at the time of the collection of the emission rate sample. The resulting emission rates are expressed in terms of the micrograms of VOC released per gram of vegetation per unit time.

To sample leaf-litter soil emissions, a stainless steel sealing ring and bag collar are used (Figure 1.1-b.). For collection of a sample the sealing ring is driven into the soil; the bag collar is then placed in the center of the sealing ring. Next, moist dirt is used as a filler between the sealing ring and the bag collar. After the collar and ring are in place, a Teflon bag vegetation enclosure is attached to the bag collar. The sample collection procedure is then identical to that for vegetation. For this type of sampling, vegetation can be clipped near

FIGURE 1.1-a

VEGETATION EMISSION SAMPLE COLLECTION SYSTEM

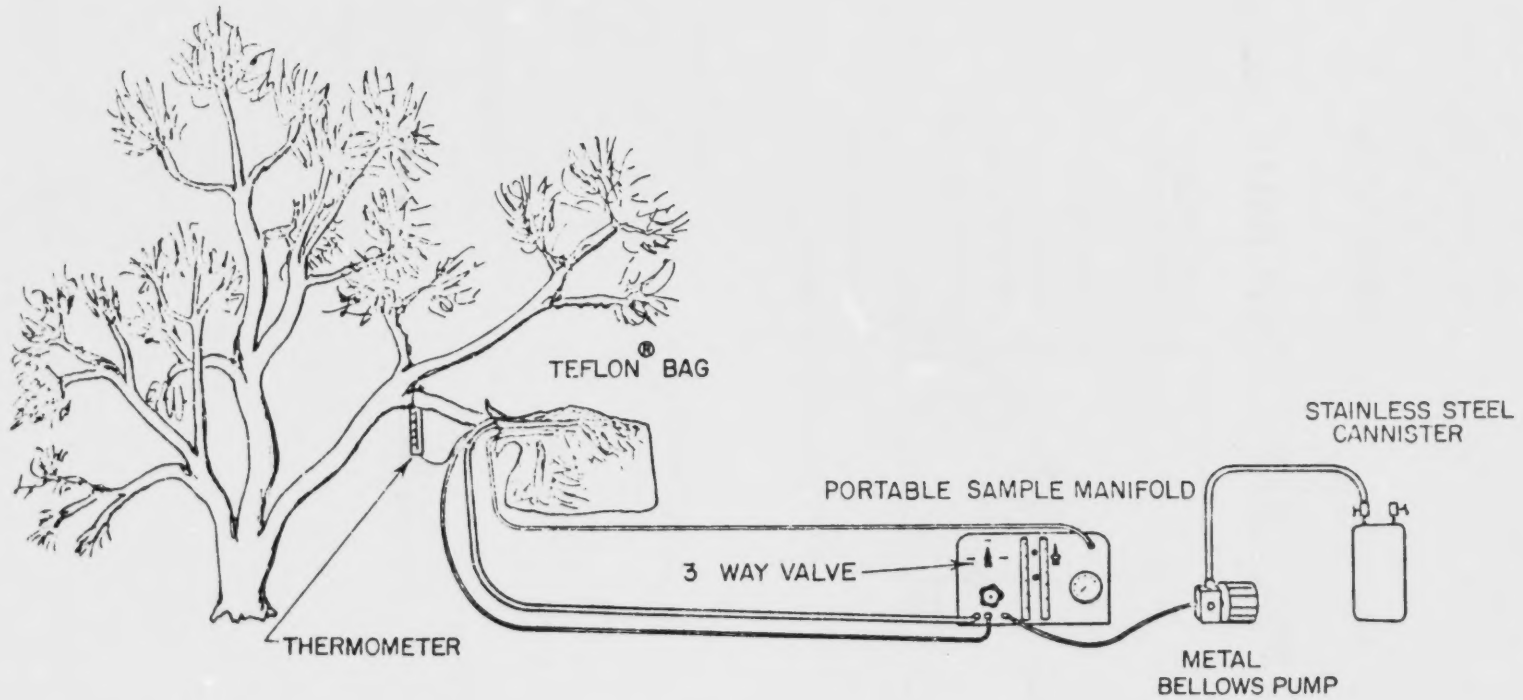
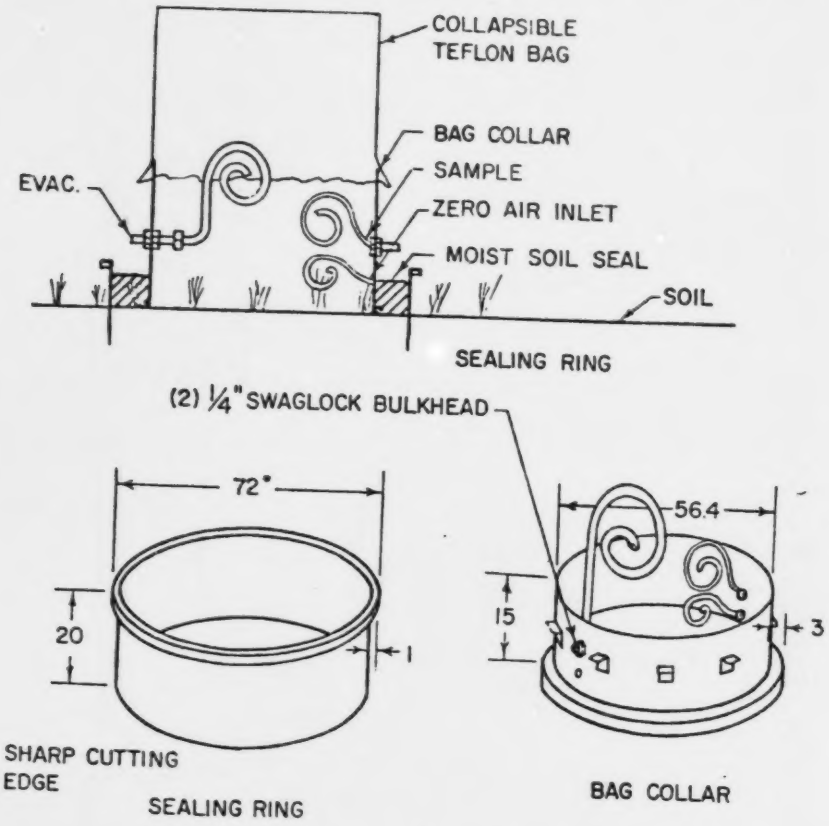


FIGURE 1.1-b

SOIL LEAF-LITTER SAMPLING SYSTEM



*all dimensions in centimeters

the ground and leaf litter collected, dried and weighed for emission rate calculations. Usually, however, it is sufficient to assume that the bag collar encloses an "average" amount of biomass material. In this case the emission rate can be directly related to the soil surface area enclosed to result in emission rate in terms of $\mu g/m^2$/minute.

Surface waters are sampled by attaching a flotation ring (consisting of two water-ski belts sewn together) around the bag collar. The bag collar, with flotation ring and Teflon enclosure bag attached, is then placed upon the surface of the water (Figure 1.1-c.). The residual air inside the bag is then quickly removed (thus collapsing the bag). Zero air is added to the enclosure in the same manner as for vegetation or soil/leaf litter sampling. No background sample is necessary, for the dead volume can be reduced to zero for these samples.

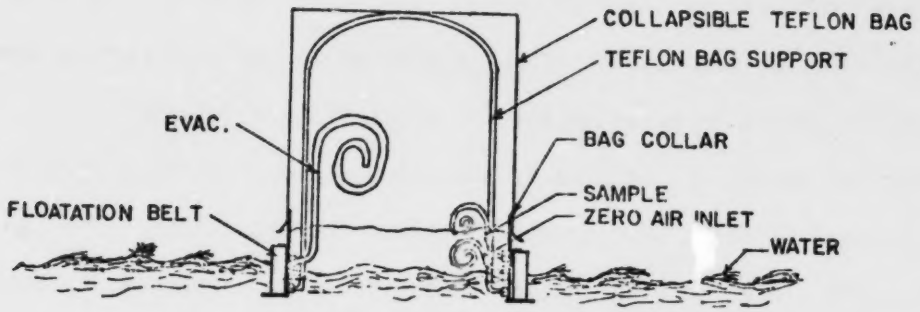
The success of these methods is based upon the short enclosure time (fifteen minutes or less) and the large amount of diluent zero (VOC free) air introduced into the enclosure. Both of these factors mitigate static chamber difficulties such as high chamber temperature and the long-term accumulation of metabolic CO_2 (from soils or from vegetation in the dark) and/or water vapor that may affect emission rates. At the same time, samples are concentrated enough to allow good analytical resolution of the hydrocarbons present.

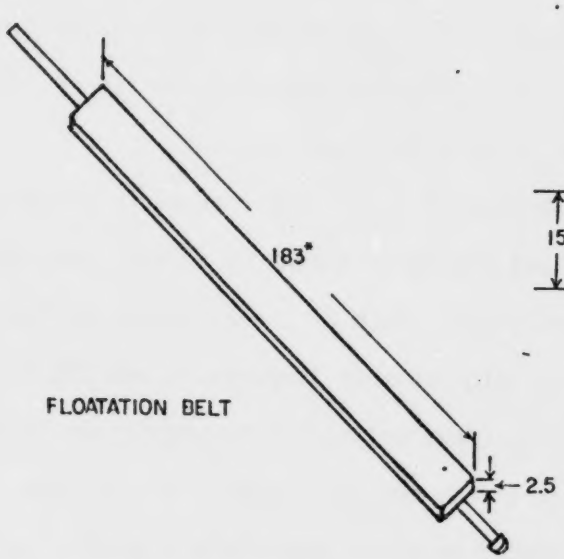
1.1.1. Sampling Equipment

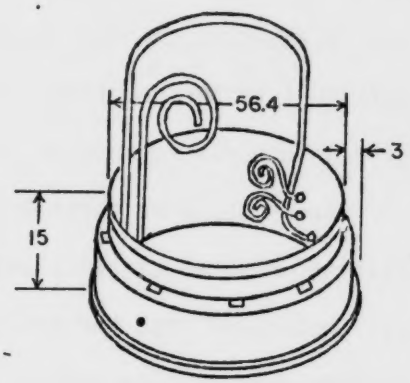
To collect emission samples from vegetation, leaf litter and water surfaces the following basic equipment is needed:

1. A portable source of pure air which is free of VOC and can be regulated to give a precise flow rate.

Figure 1.1-c. SURFACE WATER SAMPLING SYSTEM







*all dimensions in centimeters

2. A vegetation enclosure which does not add to or take away from organic vegetation emissions.

3. A method to collect an air sample from the enclosure and to move it to the laboratory for analysis.

4. A method to measure the amount of the air sample which is collected .

There are primarily two sources of VOC free "zero" air:

1. commercially available cylinders

2. zero-air generating equipment which purifies ambient air

Commercially available cylinders have the advantages of being easy to obtain and they require a relatively small investment. Their disadvantages are that they may contain relatively high level of VOC (up to 1 ppm) and unknown quantities of CO, CO_2, and NO_x. Also, the N_2/O_2 ratio is not constant from tank to tank.

Equipment is available which can manufacture zero air from ambient air on a day-to-day basis. The Aadco air generator is an example. The main advantage of the zero air generator is that it can produce a continuous supply of air of uniform quality characterized by a constant N_2/O_2 ratio. However, the equipment is not portable, so methods must be provided to get zero air from the laboratory to the field.

The zero air produced by the Aadco pure air generator has no detectable hydrocarbons or fluorocarbons. It has a CO_2 level of about 10 ppm. An ascarite (sodium hydroxide-asbestos) trap can be added to the output stream to adsorb CO_2. It may be desirable to add CO_2 to reach a concentration of about 365 ppm representative of ambient air. The major disadvantages of a zero air generator are the higher initial purchase

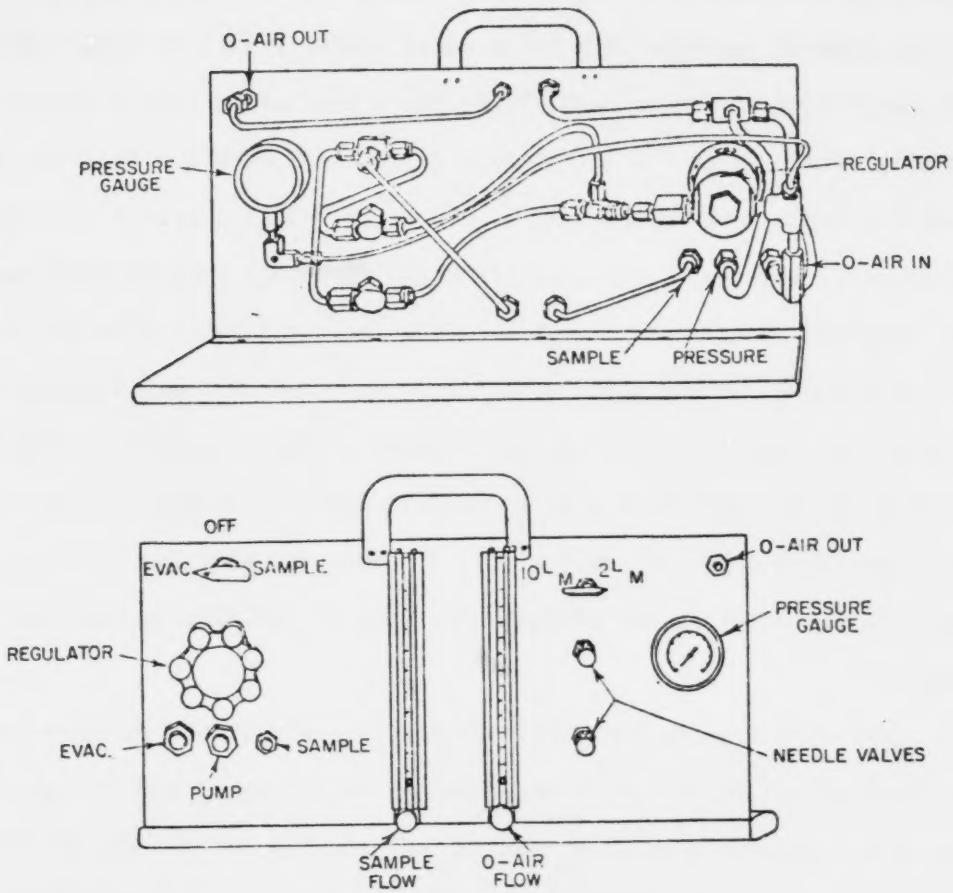
price than cylinder air and the lack of portability. WSU's method of providing a portable source of zero air is to cryogenically collect the output from the zero air generator into empty high pressure medical-grade oxygen cylinders. The procedure is outlined in the documentation portion of this manual. Approximately 100 ℓ of zero air is required per vegetation sample collected.

Regardless of the source of zero air, the result will usually be packaged in a high pressure cylinder. The cylinder must then be pressure-regulated and flow-controlled. The apparatus used in this study is shown in Figure 1.1-d and consists of a 300 ℓ cylinder of zero air connected to a pressure regulator which contributes no background VOC to the sample. The regulator is in turn connected to a pressure gauge and to a three-way valve which is connected to two needle valves. One is pre-set to give a flow of 10 ℓ/min and the other is set to give a flow of 2 ℓ/min at a specified outlet pressure (40 psig). Thus a flow of 10 ℓ/min or a flow of 2 ℓ/min can be selected by positioning the three-way valve. Possible alternatives to high pressure cylinders include the use of large, clean, 100 ℓ capacity Teflon bags filled with zero air, plus the appropriate D.C. pump and flow controllers to attain the flow rates specified in the sampling procedures. Large low pressure (air compressor type) tanks could also be used to hold the zero air needed for sampling.

The vegetation enclosure which has proven to be the easiest to work with is a Teflon bag. The bag should be closed on three sides. The dimensions are not critical; however, enclosure bags should be constructed so that they have a capacity of at least 120 ℓ when fully inflated. The one used in this program measured 109 cm x 144 cm. These bags can easily be

FIGURE 1.1-d

PORTABLE SAMPLE MANIFOLD



fabricated in most laboratories. No special fittings for sample probes are required.

There are a number of methods for removing an air sample from the Teflon bag enclosure and pressurizing it into a stainless steel canister. The simplest, most direct method is to use a metal bellows-type pump equipped with a DC motor and a Teflon valve assembly. (Note: Teflon must be specified at the time of purchase or a Viton valve assembly will be installed by the manufacturer. Under heat, Viton has a high bleed rate of organics.) An alternative is to use a cryogenic collection technique in which the sample container is immersed in liquid N_2 to "pump" a sample into the container. Special, large capacity stainless steel wide-mouthed dewars are required to hold the liquid N_2. The least desirable alternative is to use a 100 ml ground glass or a large gas-tight syringe to remove a sample and place it in the sample container. The procedure is slow and chances for contamination are increased. Whatever method is used, it must provide a means of pressurizing a sample container or filling a small Teflon sampling bag without adding to or subtracting from the sample.

Specially treated SUMMA-passivated stainless steel canisters having an internal volume of 5.5. ℓ were used as sample containers in this study. The SUMMA process is an electropolishing procedure which removes the active sites from stainless steel, thus minimizing the adsorption of organics from the sample. The "cans" are easy to clean by heating and purging with a clean gas (such as zero air). WSU has tested the storage characteristics of the electropolished stainless steel canisters and has found that the total non-methane hydrocarbon (TNMHC) concentrations are

stable in the cans; however, the ratios of some reactive hydrocarbons such as isoprene may change over a period of days in some of the cans. Emission samples have been stored for up to a week with no noticeable change in the hydrocarbon composition. Teflon sample bags could be used as sample containers if they are kept out of direct sunlight after filling and their contents are analyzed within a matter of hours after collection.

Another possible method of sample collection is to outfit a freeze-out loop with "quick disconnect" fittings and directly freeze out the sample. This method has several disadvantages. The loops must be kept in liquid N_2 from sample collection to analysis. Also, only one analysis per sample is available.

If analysis of a specific compound was desired, a solid absorbent such as Tenax could be used for sample collection. However, the method would also allow only one analysis per sample. Additionally, the adsorption-desorption efficiency of Tenax vaires from compound to compound, and a quantitative broad spectrum analysis would be difficult.

Miscellaneous other sampling equipment is needed in field testing. An inexpensive indoor-outdoor thermometer can be used to measure bag temperatures and ambient air temperature simultaneously. This works well because the outdoor temperature sensor can be placed along the branch inside the sample chamber, and the thermometers can then be hung in a convenient location on a tree limb. The temperature sensors should not be placed in direct sunlight or erroneous reading will result.

If sample canisters are used, a pressure gauge is required. The pressure gauge should be equipped with a side-port needle. One valve of the sample canister should be equipped with a Teflon-backed silicon rubber

septum. When a pressure reading is required, the pressure gauge needle is inserted through the septum and the canister valve cracked open.

Relative humidity and other miscellaneous sensors can be added to the sampling instrumentation. However, the materials of construction of each of these should be carefully checked to insure that they do not affect the sample integrity.

Clean copper tubing is acceptable for use as sample probes and zero air probes. All tubing should be thoroughly cleaned before use. The copper tubing can be slowly purged with an inert gas such as clean nitrogen at ~10 ml/minute, and flamed using a propane torch. The tubing should be flamed starting at the purge gas inlet and should gradually proceed to the outlet end. The purge flow should continue until the tubing has cooled. The tubing can then be purged overnight with "zero air". Teflon tubing has also been used in the sample train with good results. However if the Teflon tubing used is suspected of being contaminated it should be replaced. Attempts at cleaning contaminated Teflon tubing are usually unsuccessful. A periodic blank analysis should be run on all components in the sample train to insure cleanliness.

1.1.2 Sampling Procedure

Before a sampling program is begun, the following steps should be completed:

1. The area of the emission inventory should be defined.
2. The major vegetative species of interest should be determined.
3. Supportive instrumentation such as the portable zero air apparatus, sample pump, sample chambers, sample containers and tubing should should be flushed with zero-air and checked for contamination.

The sites to be selected for vegetation sampling will be dictated by distribution and location of major vegetative species as well as by practical sampling considerations. Sites which are located away from high anthropogenic concentrations are preferred though not mandatory. The site for each vegetation sample should be selected so that it is representative of the vegetation type for the area defined. The vegetation specimen should be examined for obvious signs of disease or injury which might cause excessive resin deposits or other modified metabolic behavior and thus result in a non-representative sample. After a site has been selected, the vehicle carrying the sampling equipment should be parked downwind of the site.

Figure 1.1-e. is the field data format which can be used for the collection of vegetation and soil-leaf litter samples. This data format has been developed so that all important sample variables are recorded in a reproducible manner. This will allow the later determination of trends in emission rates as correlated with site variables and weather patterns. It also provides an orderly outline for collection of the sample, and insures that data critical to the calculation of emission rates is recorded.

The following is an instructional outline for collection of an emission sample from vegetation:

1. Record the site location, sample number, weather and the specimen description.

2. Place the sample probe, purge and flush tube, and the bag temperature sensor along the branch. They should be positioned so that they will not interfere with the bag placement. They should then be fastened in place. Strips of "Velcro" have been successfully used as fastening material for probes, sensors and bag sealing by WSU.

Figure 1.1-e. Field data format

Date 6-13 Sample # RTP Can # 148 Background 204 Emission

Location Approximately 5 mi SE Umstead Park, NC Barom _____

Sample type: White Oak

Enclosure: Teflon Bag (new)

Site description: Mixed hardwood in Piedmont area next to powerline easement (open canopy)

Weather, general: clear, warm, little wind

Weather, site shade Cloud cover 0% Ha (ambient air temp.) 31°C

Wind: direction NW Speed 0-5 Gust 7

Vegetation: describe type, age, physiological state. About 60 years old. In fair shape. Some insect damage, 8" DBH about 30' tall.

Litter: Type about 5 cm litter and duff

Incorporation --------- Depth ----------

Soil: Moisture damp ph ------ Temp. --------

Describe ----------

Time at encl. T_1 1249 T_1 End Bkdg sample 1257 start flush, T_2 1258

End flush, T_3 1304, Start sample, T_5 1304 End sample, T_6 1307

Sample rate ℓ/min. 2 ℓ/min.

Flush flow rate Z_f(ℓ/min.) 10 Purge flow rate Z_p(ℓ/min.) 2

Enclosure sample temp. 32°C (est.) Can pressure 15 psig

Comments: 30% of leaves have insect damage

Close to road

Estimated dead volume 20 ℓ

Dimensions 18" X 2" X 36"

3. Turn the Teflon bag enclosure inside-out, open the unsealed edge and alternately fill and deflate it with ambient air. This will insure that any car exhaust components accumulated during transit will be flushed out.

4. Gently slide the Teflon bag over the branch. Take care not to break twigs or crush foliage.

5. Seal the base of the bag around the branch. A 1.2 cm wide by 20 cm strip of Velcro works as a bag sealer. The Velcro is wrapped tightly around the base of the bag so that the "hook" side and the fuzzy sides overlap.

6. Record the time at the beginning of enclosure. Pump the residual air in the bag out until the bag starts to collapse around the branch. Then collect a sample of the residual air by pumping it into a sample container. This is the background sample.

7. Record the time at the end of the background sample collection.

8. Measure the rough dimensions of the partially collapsed bag and record the geometric shape that it approximates. The residual air left in the bag is the dead-volume (Ve). The dimensional information is used to aid in the estimation of the dead volume.

9. Start the 10 ℓ/minute flush, record the time. Continue the flush for 6 minutes.

10. Start the 2 ℓ/minute purge, record the time. Immediately begin collecting the emission sample, record the time. Be sure that the sample rate is less than $\sim$2 ℓ/minute.

11. Record the pressure of the sample cans. This is unnecessary if the cans have been evacuated. However if they have zero air in them them the pressure must be measured so that the dilution volume can be calculated.

12. Record the ambient temperature and the bag temperature.

13. If the same branch is to be sampled again at a later time, tag the branch at the point where the bag was sealed.

14. If the branch is not to be resampled, clip the branch at the point at which the bag was sealed. Placed the clipped branch in a paper bag and take to the laboratory.

For leaf-litter/soil samples the sealing ring is driven into the ground first. Then the bag collar is placed inside the sealing ring and the bag is attached. For surface-water samples a flotation ring is strapped to the bag collar before the bag is attached. For both leaf-litter/soil samples and surface water, evacuation, sample collection and zero air lines are connected directly to the bag collar. The temperature sensor is then placed inside the bag collar from the underside. The Teflon bag enclosure can then strapped to the bag collar. A heavy piece of elastic belting wrapped around the bag and bag collar provides a good seal. Steps 6-12 of the vegetation sampling procedure are then followed with the possible exemptions of steps 6-8, if after the bag is collapsed the dead volume is equal to zero. This condition normally occurs for surface-water samples.

1.1.2.1 Bag Blank--If it is suspected that the Teflon bag or other component of the sample train is emitting organics which compromise the sample, a bag blank can be collected. The procedure used is identical to that for collecting a vegetation emission sample, except that no branch is enclosed, and no sample is collected before the purge and flush cycles since the bag can be completely collapsed and the dead volume is zero (Ve=0).

1.1.2.2 Ambient Air Samples--It may be desirable to collect an ambient air sample at the emission sample site. The ambient air sample should be collected at the time of the bag enclosure. The collection should be integrated over a five to ten minute time period. If a local anthropogenic source is near, such as a highway, integration will minimize the chances of a non-representative sample due to a passing car, etc. If a bag blank and an ambient air sample are collected it is usually not necessary to collect a sample of the enclosed air before the flush and purge cycles (background sample). However it is still necessary to estimate the dead volume (Ve) of the enclosure.

1.2 ANALYTICAL INSTRUMENTATION AND PROCEDURE

Analytical instrumentation required for routine samples depends upon the purpose of the sample program. If total hydrocarbon measurements or total non-methane organic carbon measurements are desirable, a series of Flame Ionization Detector equipped gas chromatographs (FID, GC) is required. The FID total hydrocarbon (THC) instruments do not provide the required accuracy for emission samples. Most commercial THC analyzers have a lower threshold near 500 ppb. WSU's experience has shown that most emission samples range between 200 ppb and 2,000 ppb which is on the lower end of the sensitivity range of THC analyzers. A better alternative to THC analyzers is the use of temperature programmed FID GC's equipped with columns to separate the components of the emission sample. One GC is required to separate C_2 to C_6 hydrocarbons, and another for the C_4 to C_{12} hydrocarbons. It may be desirable to have a third GC equipped to measure methane, ethylene, ethane and acetylene.

The columns and operating conditions used in this study are given in Table 1.2-a. Sample chromatograms are shown in Figures 1.2-a and 1.2-b. The gas chromatograph and mass spectrometer can be combined in a GC-MS system to positively identify individual VOC peaks and/or as a comparison with the GC quantitation. Identical GC columns and conditions should be used in the GC and GC-MS systems so that direct comparisons can be made with respect to component elution time.

The analysis and quantitation of oxygenates is more difficult than that for pure (non-oxygenated) hydrocabons. The experiments have shown that some oxygenates may be partially lost in the sampling train (see Appendix A). In addition, although oxygenates cause a response on an FID-GC, their response factors are not necessarily the same or as great as the response factors obtained for typical paraffins, olefins and terpenes. Also they do not elute from all column types. If their retention times are known and the compounds can be identified, they can be calibrated on an individual basis. Otherwise, the oxygenates which elute will be quantitated as hydrocarbons and some error due to differing response factors will result. For the samples collected in this study, oxygenates do not apear to be a major emittant. Table 1.2-a includes the column types and GC parameters used for oxygenate analysis. Column 3 also works well for terpene compounds, although separation is superior with the glass capillary column.

1.2.1 Calibration

The C_2 analyses were calibrated using Scott standard # 54 containing ethane, ethylene and acetylene and a specially prepared Scott standard which contains these components plus methane. The area responses for each

Table 1.2-a. VOC ANALYSIS CONDITIONS

Compound	Instrument	Operating Conditions
Ethylene Ethane Acetylene	P.E. 3920 Isothermal FID GC	1. Column: 10' x 1/8" OD Porapak Q Carrier: He 80 psig, 7 ml/min. Hydrogen: 22 psig Compressed Air: 50 psig Oven: 65° (30°C for CH_4) Total Run Time: 10 min. Sample Size: 100 ml (5 ml for CH_4)
Light Hydrocarbon C_2-C_6	P.E. 3920 Temp. Prog. FID GC	2. Column: 20' x 1/16" OD Durapak N-Octane Carrier: He 90 psig, 6 ml/min Hydrogen: 40 psig Compressed Air: 50 psig Oven: -70°C to 65°C Delay time: 4 min Program rate: 16°/min. Total Run Time: 40 min Sample size: 500 ml
Heavy Hydrocarbon and Oxygenates C_4-C_{12}		3. Column: 10' x 1/18" Durapak Low-K carbowax 400 Carrier: He 90 psig, 8 ml/min. Hydrogen: 40 psig Compressed air: 50 psig Oven: -20 to 100#C Delay Time: 2 min. Program Rate; 8°/min. Total Run Time: 20 min Sample size: 500 ml
Heavy Hydrocarbon C_4-C_{12}	P.E..3920 Temp. Prog. FID GC	4. Column: 200' SCOT OV-101 with 10' x 1/16" OD Durapak Low-K, Carbowax 400 precolumn Carrier: He 90 psig, 5 ml/min Hydrogen: 40 psig Compressed Air: 50 psig Oven: 0°C to 100° Temp. Prog. Delay Time: 6 min. Program rate: 6°/min Total Run Time: 60 min. Sample size: 500ml
		5. Column: 30 m SE 30 Glass Capillary Column Carrier: He 90 psig, 1 ml/min. Oven: -30 to 80°C Temp. Prog. Delay Time: 8 min. Program Time: 4°/min Total Run Time: 50 min. Sample size: 500 ml

Figure 1.2-a. Typical analysis of a vegetation sample (Juniper)

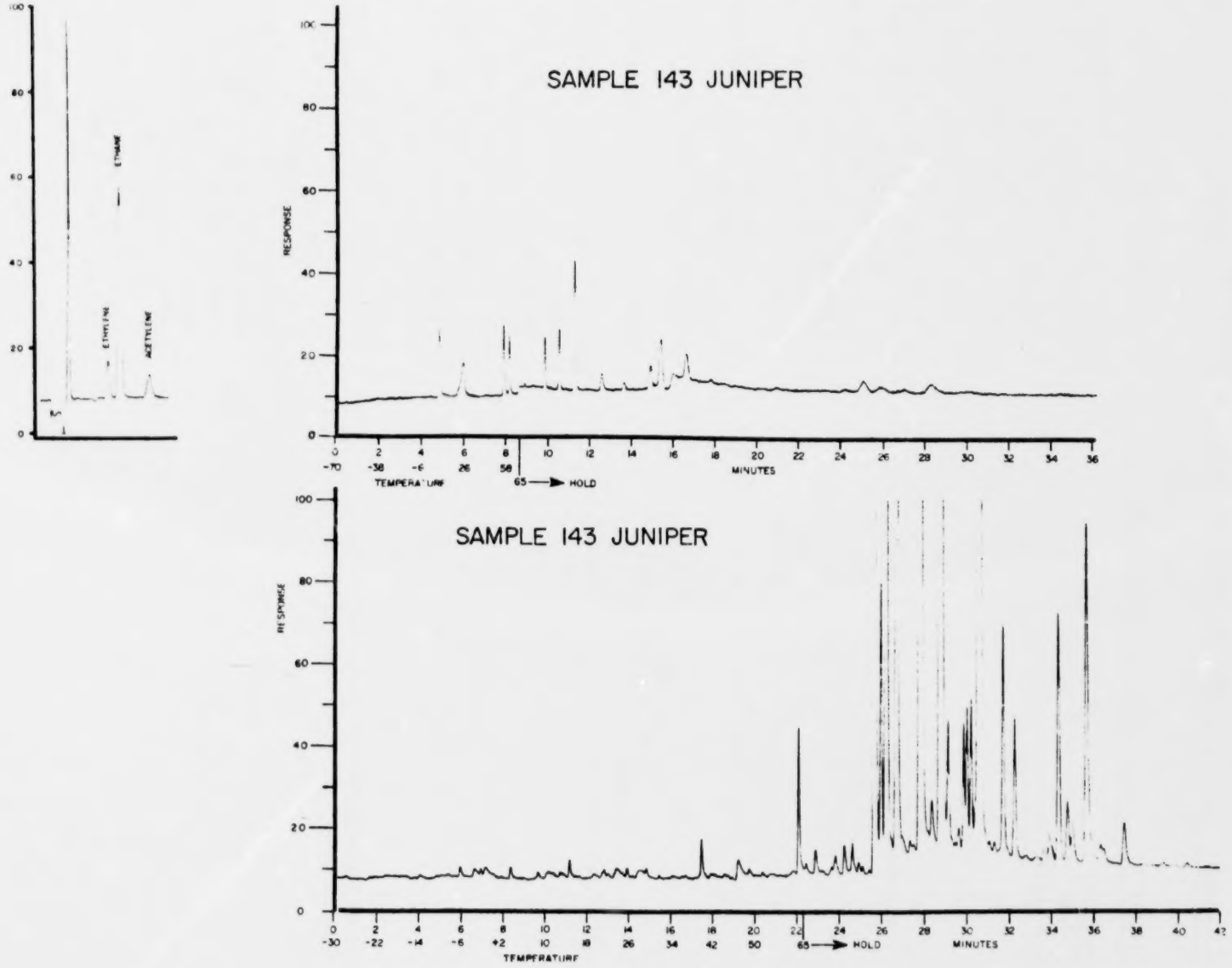
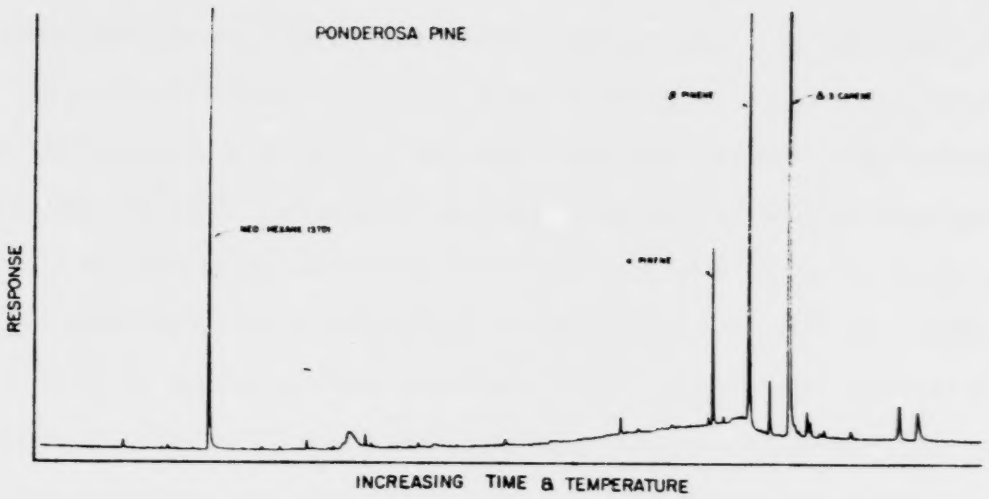


Figure 1.2-b. Sample chromatogram, glass capillary column (#5)



unknown peak in the sample are proportional to the standard concentration on a peak area basis. When an integrator is not available, peak height proportions can be compared with the peak heights of each compound in the standard. The concentrations calculated are therefore in the units of $\mu g/m^3$ for each compound.

The other GC's were routinely calibrated using a neo-hexane standard (0.209 ppm) prepared by Scott Research, Inc. Five milliliters of this standard were injected into the freeze-out loop using a pressure-lok® syringe manufactured by Precision Sampling Corporation. This was followed by 100 ml of zero air to insure that the sample was frozen out in a concentrated "slug" in the freeze-out loop. The light hydrocarbon GC was then run isothermally at 65°C until the neo-hexane peak appeared. The heavy hydrocarbon GC was temperature-programmed from -30°C to 65°C until the neo-hexane eluted. The area of the peak was integrated and the response was calculated with respect to nanograms neo-hexane/area response.

All concentrations and emission rates in this report are in terms of µg of compound. Therefore volatile organic compounds (VOC) refers to volatile organic carbon compounds. Table 1.2-b. illustrates the differences between some common methods of organic compound quantitation. It was assumed in this study that all VOC measured had an FID response equal to the FID response to neo-hexane.

Periodically a qualtitative standard was analyzed. This standard was prepared by adding concentrated microliter amounts of specific compounds to a volume of zero air or ultrapure helium in a stainless steel canister. After one or two compounds were added, the standard was analyzed and the

Table 1.2-b. COMPARISON OF EQUIVALENT UNITS OF VOC QUANTITATION

Units	Methane (CH_4)	Isoprene (C_5H_8)	Terpenes ($C_{10}H_{16}$)
Molecular weight (MW) compound (g/mole)	16	68	136
Weight of carbon (CW) (g/mole)	12	60	120
Ratio of MW to CW	0.750	0.882	0.882
$\mu g/m^3$ compound	1	1	1
$\mu g/m^3$ carbon	0.750	0.882	0.882
*ppb v/v compound	1.528	0.360	0.180
*ppb v/v carbon	1.528	1.80	1.80
+ppb wt/wt compound	0.844	0.844	0.844
+ppb wt/wt carbon	0.633	0.744	0.744

*at 25°C and 760 mm Hg
+Density of dry air = 1185 g/m^3

Note: To convert the compounds listed from $\mu g/m^3$ to another unit of measure in the bottom part of this table, multiply by the number in the appropriate column.

peaks were labeled. Gradually a wide range of compounds were introduced, one or two at a time, and their elution times identified chromatographically. The procedure can result in a mixture of the full range of compounds expected in the samples to be analyzed. The unknown samples are then analyzed and tentatively identified by matching elution times with those of the standard. This tentative identification can be confirmed using a GC-MS system.

1.2.2 Sample Enrichment

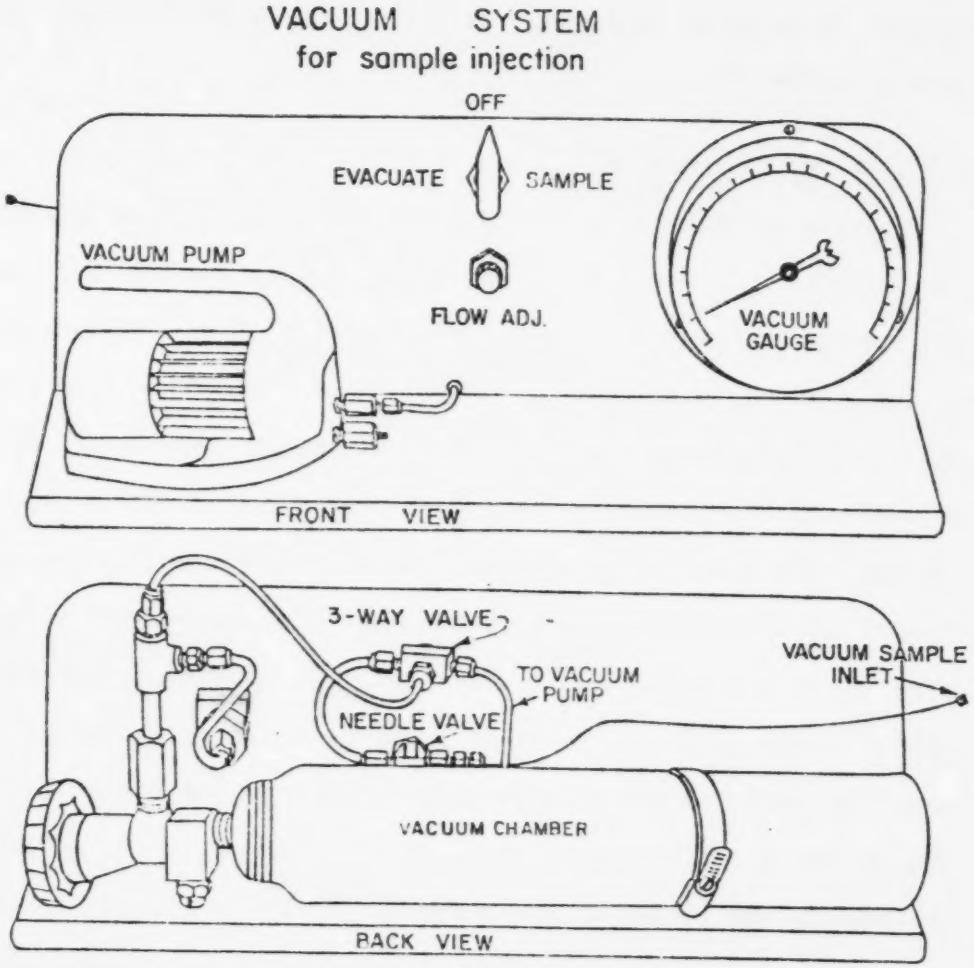
It is necessary to use a sample size of up to 500 ml for biogenic emission samples and up to 1000 ml for ambient air samples to obtain the required gas chromatographic response. This sample size is too large to inject directly into the GC and will overload the columns and destroy their resolution capabilities. Therefore a standarized sample enrichment step is necessary. The preferred method is the freeze-out technique. With this method a 3.2 mm (1/8") o.d. stainless-steel loop filled with 60-80 mesh glass beads is connected to a six-port sampling valve. When concentrating a sample, the loop is immersed in liquid oxygen. The sample is then pulled through the loop by a calibrated vacuum system or injected into the loop with a 100 ml ground glass syringe. All of the organics are retained on the glass beads while the nitrogen and some of the oxygen pass through. The valve is then switched. This causes the gas chromatograph carrier gas to be introduced from the reverse direction of that which the sample entered. At the same time, the loop is immersed in hot water. This procedure flushes the contents of the loop onto the head of the column in a concentrated slug and results in excellent resolution and sensitivity.

Several solid adsorbents are available as sample concentrators; however, WSU has found that they are usually satisfactory for only specific hydrocarbons, sometimes contribute background bleed peaks to the sample, and require extremely careful sample introductions and temperature control to get reproducible results. The freeze-out loop method of sample concentration is preferred because of its simplicity, quantitativeness and proven reliability.

1.2.3 Sample Introduction

Sample introduction into the freeze-out loop can be accomplished by two methods. One method utilizes a 100 ml syringe and side-port needle. The syringe is inserted through a Teflon-backed silicon rubber septum placed over the sample canister valve opening. The 100 ml sample is drawn out and forced through the liquid oxygen-immersed sample loop. This procedure is repeated until the desired sample size of 500 to 1000 ml is reached. The other method involves the use of a vacuum sampling system (Figure 1.2-c). This system uses a chamber of known internal volume which has been evacuated. The vacuum gauge is attached to the chamber and calibrated so that a specified change in vacuum is equivalent to a specified sample volume. The evacuated chamber is located on the down stream side of the freeze-out trap, and therefore it cannot contaminate the sample. The vacuum pulls the sample from the sample canister through the freeze-out loop where the organics are trapped. If the vacuum system is used, the sample volume does not require correction to STP. However, if the standard is injected via syringe, it must be corrected to STP since the volume of the syringe is affected by the daily barometric pressure.

FIGURE 1.2-c


VACUUM SYSTEM
for sample injection
OFF
EVACUATE
SAMPLE
VACUUM PUMP
FLOW ADJ.
VACUUM GAUGE
FRONT VIEW
3-WAY VALVE
TO VACUUM PUMP
VACUUM SAMPLE INLET
NEEDLE VALVE
VACUUM CHAMBER
BACK VIEW

1.2.4 Analysis

The samples should be analyzed as soon as possible after collection. It is desirable to analyze the emission sample first, then the background, ambient air and bag blank samples (if collected), in that order. Ratios of the components of a sample may vary with time; however, WSU's experience during this study showed that the VOC in the sampling canisters will not vary by more than 15% after a storage of several days.

1.2.5 Emission Rate Quantitation

The light hydrocarbon analysis provides good component separation for hydrocarbons in the C_2 - C_6 range. Samples of 500 ml or larger, which were collected under very humid conditions or wet samples which are introduced into the freeze-out trap through the potassium carbonate dryer at too fast a rate, may cause ethylene to elute as an unquantifiable peak. In those cases ethylene, ethane and acetylene values are obtained by analyzing the sample on the Porapak "N" column. Methane can also be quantified on this column by simply filling the sample loop (no sample concentration step) and injecting isothermally at 30°C.

The heavy hydrocarbon analysis provides quantitation for C_4 - C_{12} hydrocarbons. To determine the non-methane VOC total, the C_4 - C_{12} totals obtained from the heavy VOC analysis are added to the C_2 - C_4 totals obtained from the light VOC analysis (and/or C_2 analysis).

1.2.6 Biomass Quantitation

After the emission sample is collected the branch should be clipped and stored in a paper bag. Then the foliage should be placed into an oven at 70°C for 3 to 4 days until it reaches a constant dry weight.

If many samples of the same species are to be collected, it may be desirable to measure the fresh weight of the sample so that the ratio of fresh weight to dry weight can be determined. This will aid in estimating tentative emission rates from branches which will be resampled at a later date and have not been clipped. After drying it may be desirable to separate the foliage into its leaf, twig and branch components, and then to weigh each. Whether leaf, twig and branch biomass, leaf biomass or some other biological parameter is used will depend upon the biomass factors available for the study area. For the emission samples collected by WSU, dry leaf biomass was used in the calculation of vegetation emission rates.

Emission testing by WSU has shown that there are no significant differences between emission rate estimates developed on the basis of leaf biomass or leaf twig and small branch ($\leq$ 4 cm O.D.) biomass. The emission rates are smaller when calculated in terms of leaf twig and small branch biomass than when calculated for leaf biomass only. But since the leaf twig and small branch biomass/unit area is larger than leaf biomass alone, the total emission factor is the same as when the emission rates are calculated in terms of leaf bimass only and multiplied by the smaller leaf biomass/unit area factor. As long as the allometric relationship between the chosen sample parameter (leaf biomass, leaf surface area, Chlorophyll content, etc.) remains constant for the species being sampled (on a ground area basis), the parameter used to relate the emission rate of the enclosed portion of a plant on a sample basis, to the emission rate on an area basis, is unimportant. The emissions from tree trunks have not been considered in this report. It was assumed

that tree trunk emissions would be insignificant compared to the emissions from leaves.

1.3 SPECIAL FIELD TESTING PRECAUTIONS

1. Be sure all sampling equipment is free of contamination before an extensive field testing program is begun. Special care should be taken to slowly purge and to heat sample loops and columns to at least 100°C between each heavy hydrocarbon analysis. Otherwise residual hydrocarbons may contaminate the next sample. This may be evidenced as large broad "ghost peaks" with peaks from the next analysis superimposed. If a syringe is used to introduce the sample into the freeze-out loop, it should be purged with zero air between G.C. runs.

2. If samples are suspected of having large amounts of moisture, use the smallest sample volume which will allow quantitation of the VOC present. Water may interfere with the light hydrocarbon (LHC) analysis. This problem can be minimized by passing the sample slowly (25 ml/min) through a 1/4" x 12" copper tube packed with potassium carbonate. The potassium carbonate will dry the LHC sample without affecting its composition or quantitation. Excessive water or an excessive rate of sample introduction through the potassium carbonate dryer will be evidenced by a poor peak shape for ethylene. The C_2 column is relatively insensitive to water. Therefore, ethylene quantitation can be obtained from the C_2 analysis if necessary.

The glass capillary column for heavy hydrocarbon analysis is also relatively insensitive to water. However, large amounts of water could strip some of the capillary coating material and result

in large rounded peaks. To date, no samples have been collected which cause this problem with the sample sizes introduced (100-500 ml.)

3. Extreme care must be taken when enclosing a branch not to break twigs or leaves. Broken surfaces tend to emit a large amount of VOC immediately and then emissions rapidly taper off. Since the background sample is collected after enclosure it will partly account for these excess emissions. However, if broken twigs are noted, it is best to abandon the selected branch and sample another.

4. After the initial flush of 60 ℓ of zero air is put in the bag (10 ℓ/min for 6 min) and the purge flow-rate is started (2 ℓ/min), the contents of the bag can be mixed by gently grasping each side of the bag and using a gentle kneading motion to stir the air inside.

5. If two consecutive samples are to be collected in short succession using the same bag, it may be desirable to turn the bag inside out for the second sample.

6. When sampling leaf-litter, it is not necessary to firmly compress the dirt between the bag collar and the sealing ring. Also, as in branch sampling, care should be taken to minimize vegetation damage.

1.4 EMISSION RATE DETERMINATION

Emission rates cannot be calculated until the following have been completed:

1. Field data recorded.
2. Each emission sample, background sample and bag blank and/or ambient air sample analyzed.
3. VOC in each sample calculated.

4. The biomass for each sample determined by drying the leaves and weighing or estimating allometrically from the dry weights of other samples.

Basically, the emission rate is equal to the mass of VOC emitted per unit time per unit biomass or surface area.

The emission rate formula used for most of the samples collected during the course of the studies reported here was:

$$ER = \frac{C_{ss}\,(Zv + Ve) - C_{sb}\,Ve}{(Sa)\,(\Delta T_1)}$$

where:

C_{ss}: ($\mu g/m^3$) equals the TNMOC measured for the emission sample

C_{sb}: ($\mu g/m^3$) equals the TNMOC measured for the background sample

Zv: (m^3) equals the total volume of zero air put into the enclosure

Sa: (g) equals the chosen biomass component of the sample

ΔT_1: (min) equals the total emission time = $T_6 - T_1$

Ve: (m^3) equals the dead volume of the bag when collapsed around the branch. It can be calculated on the basis of the dilution of a marker component. If, for example c_b is equal to the concentration of acetylene in the background sample and c_s is the concentration in the emission sample, then:

$$Ve = \frac{Zv}{(c_b/c_s)-1}$$

The resulting emission rate (ER) developed is in terms of micrograms of non-methane VOC emitted per minute per gram of vegetation or per square meter of litter. (Note that any set of units, either on a mass or area basis, can be used if the appropriate values of Sa are substituted in the equation for ER.)

The emission rate formula described in the main text (Section 1.4) applies only to samples collected using a collapsable chamber (Teflon bag) and sample containers which have a very small dead volume such as evacuated stainless steel canisters, Teflon bags, and adsorbent traps. Appendix B shows the derivation of the emission rate equation and illustrates the formulas used to calculate emission rates when the basic sampling procedure is not followed.

It should be noted that the above emission factor development is based on the following assumptions:

1. The enclosure contents are evenly mixed prior to sampling.
2. Enclosure volume and concentration are constant over the short sampling time.
3. The enclosure is at ambient pressure.

2. EMISSION INVENTORY DEVELOPMENT

2.1 GENERAL

To be useful, the emission factors developed through use of the procedures outlined in Chapter 1 should be incorporated into an inventory. Such an inventory can be used to estimate spatial and temporal emission patterns and emission densities that can, together with other kinds of information, be used in oxidant control strategy development.

Basically, three components are necessary for inventory development: (1) a set of representative emission factors for the vegetative species, leaf litter and water surfaces in the area, (2) an indication of the conditions (season, temperature, etc.) that prevail for the time interval of interest and (3) biomass density factors, which are a measure of the quantity of vegetation or litter present in the the area. In this sense, inventorying vegetation is analogous to any other area source category, i.e., an appropriate emission factor is multiplied by some source activity level in order to estimate emissions.

As with any other source category, the same limitations must be recognized when preparing and using the vegetation emission inventory. First, most emission factors are generally only estimates of emissions for a particular set of conditions. i.e., those that prevailed during the actual source testing. In this study, most of the testing was done during the summer and fall. Only limited testing was conducted at cold

temperatures and on dormant or dead plants. Second, the biomass factors themselves (derived from the literature or developed from actual field surveys) are generally only approximations, the variability of which depends on the method used to derive them and the area to which they are applied. Third, various types of errors are always unavoidable in any program involving physical and statistical sampling. These include the imprecision and inaccuracy that are associated with the sampling and analytical procedures as well as the sampling error that results from using limited data bases to estimate the characteristics of entire populations.

2.2 LEAF BIOMASS DENSITY FACTORS

All of the vegetation emission rates used in this report are calculated in terms of leaf biomass. In other words, it was assumed that the emission rates for each vegetation sample would be proportional to the dry weight of the leaves present. It was further assumed that this emission rate relationship would not change when extrapolating the sample emission rates to larger area emission factors. To calculate vegetative emissions over some area of interest, these sample emission rates ($\mu g/g \cdot hr$) must be multipled times approximate indicators of the amount of leaf biomass present per some unit of area, i.e., leaf biomass density factors (g/m^2). The result is an area wide emission factor ($\mu g/m^2 \cdot hr$). Leaf biomass density was selected as the most appropriate indicator for the following reasons:

1. A broad and well-defined data base exists for leaf biomass density factors which can be applied to regional or area specific emission inventories (Lieth and Whittaker, 1975; NAS, 1975).

2. Leaf biomass is easily measured in the field for emmision rate samples. The measurements require no special equipment or training to complete. The averages of sample emission rates can then be directly multiplied by leaf biomass densities to result in area emission factors. (The emission rates for leaf litter or water surfaces are simply multiplied times the area covered to estimate emissions).

3. Leaf biomass densities for many forest types tend to be uniform over broad areas and are relatively insensitive to site-specific variables (Satoo, 1967; Bazilevich, et al., 1968).

Much of the data concerning the dynamics of biomass distribution within various ecosystems has been generated as the result of investigations carried out under auspices of the International Biological Program (IBP). The IBP was a multinational, multidisciplinary program with the ultimate goals of developing ecosystem models by reducing the interactions of environmental factors into a series of mathematical relationships. These models could then be used to predict the impact of various land use options upon specific ecosystems. One of the achievements of the IBP program was the formation of various models to predict the primary productivity or the amount of carbon formed for various land and vegetation types. In order to develop these models, fieldwork was conducted to harvest tree species for various forest types and to quantify each component.

The results of these studies, conducted in countries throughout the world and at 21 research sites in the United States, were used in this report to estimate leaf biomass densities so that an example VOC emission inventory for the U.S. could be compiled.

The estimation of leaf biomass density factors is made easier because the amount of leaves over a given area of ground is fairly independent of the type of vegetation and the age of vegetation (Lieth and Whittaker, 1975). Many authors have also reported that stand density, after canopy closure, does not affect the leaf biomass per ground area (Satoo, 1967). It has further been reported that the leaf biomass density of many dissimilar types of vegetation from grassy savannas and subtropical rain forests to northern and middle Tiaga coniferous forests range from 600 to 1250 g/m^2 (Bazilevich, et al., 1969). Leaf biomass density factors for the United States seem to range from 100 g/m^2 for extreme desert conditions to 1100 g/m^2 for the most productive rain forests (NAS, 1975).

An additional advantage of using leaf biomass density in compiling an emission inventory is the availability of locally or regionally specific information for detailed emission inventories. Local sources of information which may be useful include agricultural crop yield reports, local forest surveys, land use planning studies, and doctoral dissertations on local ecosystem types. IBP publications such as Primary Productivity of the Biosphere, (Lieth and Whittaker, 1975) supplement this information with conversion factors which can be used to arrive at leaf biomass densities.

The IBP classification system for specific land forms and vegetation types incoporates the concept of "biomes". Biome classifications are based upon the composition of the potential vegetation (before disturbance by man), the physiography and physiognomy of the land and on the climate of the area. Many of the biome names correspond to types of vegetation (i.e., Deciduous Forest Biome or Coniferous Forest Biome), however, their classification is independent of transient vegetation types such as hardwoods or conifers. For this reason, although Pine plantations

have rapidly replaced many hardwood stands in the Southeast United States, the area is still classified due to its potential vegetation, land form, and climate as a Deciduous Forest Biome. Figure 2.2-a illustrates a generalized biome composition for the Continental U.S. The numbers on the map identify each biome so that their areas can be estimated (Table 2.2-a).

2.3 EMISSION RATE ALGORITHMS

Early in the research program it was recognized that certain sample variables seemed to affect emission rates. Terpene type emissions tended to be greater at higher temperatures, low elevations and early in the growing season than emissions collected at low temperatures, high elevations or late in the fall. Rasmussen (1970) indicated that isoprene was only emitted by certain plants and only in the light. The field measurements in this study confirmed this light dependency for isoprene emissions. The variability of the field data indicates that although trends are present, many other sample factors could affect emission rates. These variables include site specific variables such as soil fertility, plant moisture, weather, individual variability, location of the sample on the tree, various pathologic conditions such as disease or injury and the age of the vegetation.

In order to more clearly estimate the effects of temperature and light on emission rates, a laboratory research program headed by Dr. D. Tingey, EPA Corvallis, has been conducted utilizing specially designed environmentally controlled chambers (Tingey, et al., 1978 a,b). Whole plants were place inside the chambers and the selected variable of temperature or light was changed while other conditions remained constant.

Figure 2.2-a. MAJOR BIOTIC REGIONS OF THE U.S.

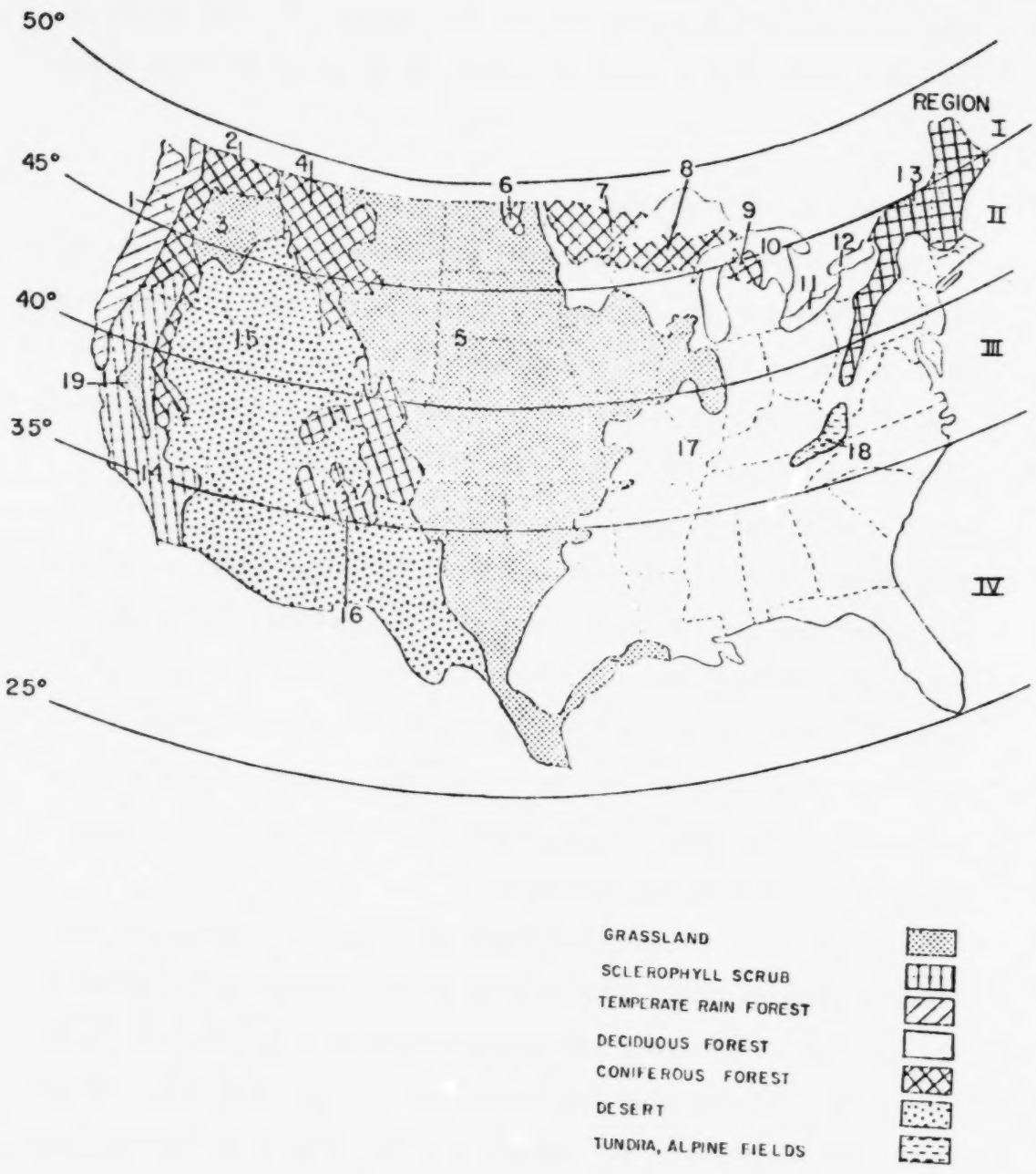


Table 2.2-a. AREAS OF THE MAJOR BIOTIC REGIONS OF THE CONTINENTAL U.S.

Biotic Region	Map No.	Area (km^2)
Temperate Grassland	3	133,577
	5	2,441,864
	19	31,375
	Total Grassland	2,606,816
Sclerophyll Scrub	14	287,162
Temperate Rain Forest	1	158,846
Deciduous Forest	17	3,105,709
Coniferous Forest	2	214,925
	4	228,922
	6	14,278
	7	108,966
	8	97,881
	9	27,054
	13	257,290
	16	243,892
	Total Coniferous Forest	1,192,892
Desert Scrub	15	1,654,681
Alpine Fields or Tundra	18	33,159
Total Continental U.S.		9.04×10^6

These experiments, completed for Live Oak, (an isoprene emitter) and Slash Pine, (a terpene emitter), indicate that there is a relationship between temperature and emission rates. For terpene emissions no light dependency could be detected. Isoprene emissions varied logarithmically with temperature. A strong light dependency was also noted for isoprene emission, however, maximum isoprene emissions were reached at fairly low intensities and increasing light intensity above this point of saturation did not increase isoprene emission rates. The study quantified the relationships between temperature and terpene emissions at any light level, between isoprene emissions and temperature at various light levels and between isoprene emissions and light at various temperatures.

For purposes of this emission inventory WSU assumed that the change in VOC emission rates with temperature for all vegetation types (except for isoprene emitters) would vary similarly to the Slash Pine studied by Tingey. WSU also assumed that changes in emission rates with temperature for isoprene emitting species would vary similarly to the Live Oak in the EPA-Corvallis study. An additional assumption was made that all isoprene emitting species were light saturated during the daylight hours. This means that emission rates might be over-estimated for leaves deep within the canopy or in very shady locations during some part of the day. For nighttime, all isoprene emission rates were assumed to be zero. Finally, WSU assumed that leaf temperature would approximate the temperature measured inside the bag during the sampling. Figure 2.3-a shows the emission rate algorithms used to calculate the respective VOC emissions. Since the field data were collected under a wide range of temperatures, a correction factor was used to standardize the VOC emissions to specified conditions of saturating light and a leaf temperature of 30°C. The

Figure 2.3-a. Emission rate algorithms

Isoprene

$$^{+}\ln (Er) = \frac{4.88}{1 + \exp [-0.18 (Ta - 25.26)]} + 0.11$$

Isoprene Temperature correction factor to 30°C:

$$Er = Er^{*} \left[\frac{34.194}{\exp \frac{4.88}{1 + \exp [-0.18 (Ta - 25.26)]} + 0.11} \right]$$

where: Er* = Isoprene emission rate (measured)
Er = Isoprene emission rate (std. to 30°C)
Ta = Leaf temperature
exp is an exponential

Terpenes

$$^{++} Er = \exp [-0.332 + 0.0729 (Ta)]$$

Terpene correction factor to 30°C:

$$Er = Er^{*} \frac{6.392}{\exp [-0.332 + 0.0729 (Ta)]}$$

where: Er* = Terpene emission rate (measured)
Er = Terpene emission rate (standardize to 30°C)
Ta = Leaf temperature
exp is an exponential

+From Tingey et al., 1978a.

++From Tingey et al., 1978b.

correction factors take the form of the ratio of Tingey's (et al., 1978a,b) predicted emission rate at 30°C to his predicted emission rate at the sampling temperature, times the emission rate which WSU measured in the field. According to the equation in Figure 2.3-a, temperature correction must take into account the temperature of the leaves themselves. Since leaf temperatures, per se, were not routinely measured in the study, an assumption had to be made concering the relationship between leaf temperatures and the measured bag and and air temperatures. From energy balance calculations it is apparent that leaf temperature and air temperature inside our enclosure during sampling are very close (Gates, 1971). The relationship between air temperature and bag temperature and leaf temperature, however, is difficult to estimate. The primary factors that affect this relationship are the size of the leaf, the energy absorption by the leaf, wind speed and transpiration rate (Gates, 1965). From our field measurements, it appears that in the morning or afternoon hours or if the sunlight is filtered through foliage or shaded by clouds, bag temperatures are within 5°C of ambient air temperatures.

Because bag temperature more accurately reflects leaf surface temperature, a probable controlling factor for emissions, the raw emission rates were specified in terms of bag temperature. When the emission rates are standardized to an ambient temperature of 30°C, the possibility of underestimating emission factors is enhanced. For instance, the emission rate measured at a bag temperature of 35°C is necessarily lowered when standardized to prevailing ambient conditions of 30°C. Under these conditions leaf surface temperatures of unenclosed as well as the enclosed vegetation are probably closer to the bag temperature than to the ambient air

temperature (Gates, 1971). Therefore, when the emission rate is standardized to an ambient air temperature of 30°C, the effect is a lower emission estimate than would be expected at a corresponding leaf surface temperature of 35°C.

Although leaf temperatures may be higher than ambient temperatures for some leaves during some period of the day, it is much more difficult to estimate average diurnal leaf temperature cycles than average diurnal air temperature cycles. For this reason, in this inventory WSU has assumed the bag temperatures equaled air temperature. It was recognized that this assumption could lead to underestimation of emission rates. This potential underestimation of emission estimates would be moderated somewhat for isoprene emitters because during periods of direct sunlight temperatures of some leaves may exceed 44°C and the leaf would then begin to physiologically shut down (Tingey, et. al., 1978a). Since isoprene emissions seem to be tied to photosynthesis (Sanadze and Kalandadze, 1966) the isoprene emission rate would be reduced for the over-heated leaves. In other words, in bright sun, leaf temperatures of some of the leaves for some broadleafed plants tend to be warmer than ambient air during some hours of the day, causing emission rates based only upon bag temperature and standardized to ambient air temperature to be too low. However, some of the leaves of a canopy may exceed temperature of 44°C, causing a sharp decrease in isoprene emission rates. These factors, therefore, may tend to balance.

The ranges, as well as the magnitudes, of emission rates from leaf litter, soil and water surfaces were much smaller than for vegetation. Their temperatures remained more uniform and no exmperimental work on emission rate algorithms had been completed. Therefore, no attempt was

made to standardize the emission rates for these categories. Additionally, for this study it was assumed that the emission rate of an enclosed branch at a specific bag temperature would be representative of the emission rate of the whole plant if the ambient temperature was equal to the bag temperature.

2.4 NATURAL EMISSION DATA

Each vegetation species exhibits a characteristic spectrum of emission components. Table 2.4-a lists the emission profiles for some species sampled in Florida. Table 2.4-b exhibits typical emission ratios of selected species sampled near Santa Barbara, CA, Pullman, WA and RTP, NC. The percentages listed are averages. The specific sample ratios vary with sampling conditions and with the individual samples; however, the major components are consistenly emitted for each vegetation type. As Table 2.4-a and 2.4-b show, the major emission components do not add up to 100%. For some samples the remainder of the total emission consisted of many small component peaks. For many samples these peaks typically eluted in the portion of the chromatogram where paraffin type compounds elute. For many of the California samples such as Mesquite and Manzanita, the emissions eluted from the GC column in the area of the chromatogram where paraffins normally elute or later in the chromatogram where some aromatic compounds and oxygenates elute. In these samples, emission components could not be matched with known standard compounds as GC-MS analysis was unavailable at the time that the samples were collected. The emission "fingerprint" of these samples was dissimilar to any other vegetation type sampled previously.

Table 2.4-a. EMISSION PROFILES FOR SELECTED FLORIDA VEGETATION

Vegetation Type	Major Emissions	Approximate Percent of non-methane VOC
All oaks (*Quercus spp.*)	Isoprene(daytime only)	90-99
Long Leaf Pine (*Pinus palustris*)	α-Pinene	30
	β-Pinene	30
	d$_3$-Limonene	2
	Δ^3-Carene	2
	Myrcene	1
	Propane	8
Slash Pine (*Pinus elliotti*)	α-Pinene	27
	β-Pinene	16
	d$_3$-Limonene	19
	Δ^3-Carene	12
Sand Pine (*Pinus clausa*)	α-Pinene	35
	β-Pinene	44
Austrailian Pine (*Casuarina equisetifolia*)	Isoprene	92
Saw Palmetto (*Serenoa repens*)	Isoprene (daytime only)	85
Sabal Palmetto (*Sabal Palmetto*)	Isoprene	90
Cypress (*Taxodium districhum*)	α-Pinene	46
	Δ^3-Carene	21
Sweet gum (*liquidumbar styraciflua*)	Isoprene	20
	α-Pinene	13
	β-Pinene	02
	d$_3$-Limonene	02
	Δ^3-Carene	06
	β-Phellandrene	51

Table 2.4-b. EMISSION PROFILES FOR SELECTED SPECIES

Vegetation Type	Major Emissions	Approximate Percent of non-methane VOC
Pullman, Washington		
Ponderosa Pine	Δ^3-Carene	36
	β-Pinene	25
	α-Pinene	14
Lombardi Poplar	Isoprene	99
Douglas Fir	α-Pinene	24
	d-Limonene	7
	β-Pinene	5
California		
Manzanita	unknown 8A	18
Chemise	unknown 4A	25
Eucalyptus	Isoprene	40
RTP, NC		
Dogwood	Δ^3-Carene	10
Yellow Poplar	d-Limonene	10
	unknown #28	8
	Terpinolene	5
American Sycamore	Isoprene	74
Eastern Red Cedar	Δ^3-Carene	52
	α-Pinene	26
Loblolly Pine	α-Pinene	35
	d-Limonene	26
	β-Pinene	19
	Δ^3-Carene	11
Shortleaf Pine	α-Pinene	53
	d-Limonene	17
	β-Pinene	12
	Δ^3-Carene	11
Virginia Pine	unknown #26	26
	α-Pinene	22
	β-Pinene	10
	d-Limonene	38
	Δ^3-Carene	2

In general, most of the species tested exhibited definite emission patterns. Oaks emitted primarily isoprene. Conifers emitted primarily terpene type compounds such as α-pinene, β-pinene and Δ^3-carene.

Table 2.4-c presents a summary of the VOC emissions for broad categories of vegetation grouped together on the basis of similarities in emission components and in emission rates. All oaks are grouped together. All conifers are also averaged. From examination of emission rate data it appears that one of the primary factors influencing emission rates is whether or not the plant is a prolific isoprene emitter. For this reason all of the non-oak isoprene emitters (where isoprene is greater than 50% of the VOC) are averaged and all of the non-oak non-isoprene emitters are averaged. Additionally, groupings were made of emission rates for leaf litter and pasture samples, marine samples, and fresh water samples. (Note that the emissions for these latter categories are expressed in terms of $\mu g/m^2 \cdot hr$, while the emission from vegetation are expressed in terms of $\mu g/g \cdot hr$.) The values in Table 2.4-c represent the collection of samples over a broad range of temperatures and seasons. The first column of data in Table 2.4-c shows the "measured" means and standard errors for the samples at actual ambient temperatures. The "standardized" column uses the same data corrected to 30°C. The "measured" Florida data for Oaks and Non-Oak Isoprene Emitters does not include samples collected at night when isoprene emissions do not occur. RTP data could not be standardized for temperature, as the probe which monitored bag temperatures malfunctioned during sampling. No sweetgum samples were included. Sweetgums have relatively large delicate leaves and it was very difficult to collect samples without causing vegetation damage. Unfortunately, this problem was not apparent until the emission rates

Table 2.4-c. NON-METHANE VOC EMISSION RATES OF BROAD VEGETATION CATEGORIES FOR VARIOUS SAMPLE SITES

		Measured		Standardized to 30°C	
Classification (units)	N	$\bar{X}$	$S\bar{X}$	$\bar{X}$	$S\bar{X}$
Confiers (μg/g·hr.)					
Pullman, WA -76	21	2.42	0.40	4.97	0.74
Pullman,-77	5	2.65	0.93	3.64	0.93
North Carolina	7	8.35	3.93	----	----
Florida	70	9.36	1.31	8.80	1.27
Oaks (μg/g·hr.)					
Pullman-76 (Dark)	2	2.55	0.53	3.00	0.61
North Carolina	3	26.8	12.26	----	----
California	3	8.60	1.25	28.7	9.76
Florida	47	22.93	3.35	21.93	4.14
Non Conifer, Non Isoprene (μg/g·hr.)					
Pullman-76	9	2.92	1.43	7.76	4.24
Pullman-77 (Sagebrush)	2	36.0	31.89	23.6	17.18
North Carolina	8	4.68	1.72	----	----
California	17	3.48	0.97	4.13	1.01
Florida	143	4.28	0.48	4.74	0.67
Non Oaks-Isoprene (μg/g·hr.)					
Pullman-76	1	38.7	---	27.7	----
Pullman-77	1	37.1	---	----	----
North Carolina	2	5.02	0.90	----	----
California	1	10.6	---	9.16	----
Florida	55	17.45	3.51		
Leaf Litter-Pasture (μg/m^2·hr.)					
Pullman	5	105.8	35.5		
California	2	262.0	80.6		
Florida	101	162.0	17.6		
Marine (μg/m^2·hr.)					
Florida	141	128.9	10.2		
Aquatic (μg/m^2·hr.)					
Florida	11	102.4	13.4		

had been calculated. The extremely high VOC content of the background samples made it necessary to estimate the dead volumes of the vegetation samples to within 0.1 liter, which was not possible. Therefore, emission rates for sweetgum could only be estimated to range from 0 to 120 μg/g·hr.

Each sample can be considered to represent an average emission rate. Since the means of each species were averaged, the variability is best expressed in terms of a standard error of the means, rather than as the standard deviation. The standard error is equal to the standard deviation divided by the square root of the number of observations.

Although there is a range of variation between emission rates of different species collected in different locations, some broad generalizations based upon the data available can be made. For instance, it is apparent that the oak emission rates for summer samples collected in Florida are similar to those for California. Emission rates for conifers in Florida and North Carolina also appear to be similar. Conifer emissions from samples collected during the fall in Pullman WA appear to be much lower. It is not presently known whether this latter difference represents species, site, or seasonal effects upon emission rates. It was assumed for this study that the lower emission rates for Pullman conifers represented seasonal effects. Based upon the limited data collected in Pullman, California and RTP, North Carolina, and the more extensive sampling conducted in Florida, generalized emission factors were determined that were estimated to be representative of broad categories of vegetation in the U.S.

Table 2.4-d shows the vegetation species composition of the samples used to determine the emission rates for the broad vegetation categories. Generalized emission factors for broad vegetation categories are shown in Table 2.4-e.

Table 2.4.d. LOCATION AND SPECIES OF SAMPLES USED IN U.S. INVENTORY

Species	Number of Samples
Non-Conifer Non-Isoprene Emitters	
Pullman	
Maple	3
American Elm	1
Weeping Willow	1
Winter Wheat	1
Dry Peas	1
Sage Brush	4
North Carolina	
Pignut Hickory	1
Mockernut Hickory	1
Dogwood	2
Yellow Poplar	2
American Beech	1
American Hornbeam	1
Sourwood	1
California	
Adenostema Fasiculatum	1
Manzanita	5
Chemise	3
Big Pod Ceanothus	4
Eucalyptus	4
Florida	
Mangrove	37
Wax Myrtle	9
Elderberry	5
Groundsel Bush	2
Persimmon	17
Dahoon Holly	3
Red Mulberry	3
Sweet Acacia	3
Viburnum	1
Oleander	1
Oranges	29
Grapefruit	16
Non-Conifer Non-Isoprene Emitters	
Florida (cont.)	
American Elm	1
Carolina Ash	1
Red Maple	9
Hickory	4
Non-Oak Isoprene Emitters	
Pullman	
Lombardy Poplar	2
North Carolina	
American Sycomore	2
California	
Eriopictyon Traskii	1
Florida	
Saw Palmetto	35
Sabal Palmetto	12
Australian Pine	1
Willow	7
Leaf Litter-Pasture	
Pullman	
Conifer Duff	5
California	
Eucalyptus-Oak	2
Florida	
Pasture	101
Aquatic	
Florida	11
Marine	
Florida	141

Table 2.4.d. LOCATION AND SPECIES OF SAMPLES USED IN U.S. INVENTORY (continue

Species	Number of Samples
Conifers	
Pullman	
Ponderosa Pine	7
Douglas Fir	8
Juniper	3
Norway Spruce	2
Blue Spruce	1
Sub Alpine Fir	1
Mugo Pine	2
Port Orford Cedar	1
Grand Fir	1
Western Larch	1
North Carolina	
Shortleaf Pine	2
Virginia Pine	1
Loblolly Pine	2
Eastern Red Cedar	2
Florida	
Slash Pine	16
Longleaf Pine	29
Sand Pine	4
Southern Red Pine	1
Cypress	20

Species	Number of Samples
Oaks	
North Carolina	
White Oak	1
Southern Red Oak	1
Blackjack Oak	1
California	
Coast Live Oak	3
Florida	
Laurel Oak	10
Water Oak	3
Turkey Oak	7
Live Oak	18
Blue Jack Oak	7
Myrtle Oak	1
Willow Oak	1

Table 2.4-e ESTIMATED EMISSION FACTORS FOR BROAD VEGETATION CLASSIFICATIONS (STANDARIZED TO 30°)

Classification (Emission rate units)	Day	Night	Winter
Conifers ($\mu g/g \cdot hr$)	8.9	8.9	3.5
Oaks ($\mu g/g \cdot hr$)	24.7	4.7	0
Non-Conifer, Non-Isoprene ($\mu g/g \cdot hr$)	4.3	4.3	0
Non-Oak, Isoprene ($\mu g/g \cdot hr$)	10.3	2.4	0
Leaf-Litter, pasture ($\mu g/m^2 \cdot hr.$)	162	162	0
*Marine ($\mu g/m^2 \cdot hr.$)	129	129	0
*Aquatic ($\mu g/m^2 \cdot hr.$)	102	102	0

*Not included in U.S. Inventory

Also, as Table 2.4-e shows, the emissions from soil leaf litter and from all deciduous vegetation types were assumed to be zero during the winter months. No field samples have been collected to confirm this assumption.

2.5 EXAMPLE NATIONWIDE EMISSION INVENTORY

2.5.1 Purpose

Although the biogenic emission rate data gathered to date are limited, it is useful to apply this data to the construction of a nation wide emission inventory. The example emission inventory serves the following purposes:

1. It illustrates the procedure involved in preparing a biogenic emission inventory.
2. It provides a raw data base subject to further refinement.
3. It illustrates the general magnitude of biogenic VOC emissions within the current limitations of state-of-the-art technology and data.

Caution should be exercised when extrapolating the emission rates determined in the study to other areas of the country. Unique species composition, environmental influences, and meteorological conditions may result in local or regional biogenic emissions that vary substantially from estimates made in this report.

Of the approximately 780 samples collected, 630 were collected between April and mid-August in the Tampa/St. Petersburg area of Florida. Twenty-five samples were collected near Santa Barbara, California in September, and approximately 100 samples were collected near Pullman, Washington during the fall months of 1976 and 1977.

Table 2.5-a gives the leaf biomass density factor for each of the broad vegetation emission rate classifications in each biome type (Figure 2.2-a). These leaf biomass density factors were determined from literature values for each biome type (Leith and Whittaker, 1975; NAS, 1975; AAAS, 1967). The approximate composition of each biome was then estimated (Rasmussen, 1972; Dasmann, 1976; Dix and Beidleman, 1969; Franklin and Dyrness, 1969; French, 1971; Preston, 1948; Society of American Foresters, 1954). The biome biomass density factor was multiplied by its relative percent composition to get the leaf biomass density factors for each broad vegetation classification in each biome.

2.5.2 Seasonal Variability

Since it is known that season, temperature and daylight affect emission rates, it is important to consider these factors when preparing an emission inventory. Upon examining monthly average weather maps in A Climatic Atlas of the U.S. (U.S. Dept. of Commerce, 1978) and noting the regularity that temperature isopleths corresponded with latitude, the U.S. was divided into four latitudinal regions as follows: Region I = 45° - 50°; II = 40° - 45°; III = 35° - 40°, IV = 25° - 35°. These are shown on the map in Figure 2.2-a. The monthly maximum, minimum and average temperature for each region were then estimated visually from monthly minimum, maximum and average temperature isopleths. In addition, based upon the climate information available in the atlas (including temperatures, solar incidence, number of frost free days, etc.), the month was designated as a summer month or a winter month for each region (Table 2.5-b). It should be emphasized that these are only very rough approximations of average temperature conditions and that site specific information, especially in mountainous terrain might vary significantly from the figures reported here.

Table 2.5-a. BIOME EMISSION FACTORS
(Standardized to 30°C)

	Leaf Biomass Density (g/m^2)	Emission Factor (ER) Day $\mu g/m^2$ hr.	Night $\mu g/m^2$ hr.	Winter $\mu g/m^2$ hr.
Grassland				
Conifer	5	44.5	44.5	17.5
Oaks	2.5	61.75	11.71	0
[1]NC-I	3.75	16.13	16.13	0
[2]NO-I	3.75	38.6	9.00	0
[3]LL	----	162	162	0
	250	32.98	243.38	17.5
Sclerophyll Scrub				
Conifer	15	133.5	133.5	52.5
Oaks	30	141	141	0
NC-NI	210	903	903	0
NO-I	45	463	24.72	0
LL	---	162	162	0
	300	2402.50	1364.22	52.5

1 Non-Conifer, Non-Isoprene Emitters

2 Non-Oak, Isoprene Emitters

3 Leaf-Litter/Soil, pasture

Table 2.5-a. (continued). BIOME EMISSION FACTORS
(Standardized to 30°C)

	Leaf Biomass Density (g/m^2)	Emission Rate (ER) Day $\mu g/m^2.hr.$	Night $\mu g/m^2.hr.$	Winter $\mu g/m^2.hr$
Temperate Rain Forest				
Conifer	990	8811	8811	3465
Oak	55	1385	258.50	0
NC-NI	22	94.6	94.6	0
NO-I	22	226.6	52.8	0
LL	---	162	162	0
	1100	10679.20	9378.9	3465
Deciduous Forest				
Confier	135	1201.5	1201.5	473
Oaks	180	4446.0	846.0	0
NC-NI	90	387	387	0
NO-I	45	463.5	108	0
LL	----	162	162	0
	450	6660	2704.5	473
Coniferous Forest				
Conifer	559	4975.10	4975.10	1957
Oak	39	963.30	183.30	0
NC-NI	26	111.80	111.80	0
NC-I	26	267.80	62.40	0
LL	---	162	162	
	650	6480.00	5494.60	1957

Table 2.5-a. (continued). BIOME EMISSION FACTORS
(Standardized to 30°C)

	Leaf Biomass Density (g/m^2)	Emission Rate (ER) Day $\mu g/m^2$ hr.	Night $\mu g/m^2$ hr.	Winter $\mu g/m^2$ hr.
Desert				
Conifer	25	222.5	222.5	88
Oaks	25	617.5	117.5	0
NC-NI	40	172.0	172	0
NC-I	10	103.0	24	0
LL	----	162	162	0
	100	1277	698	88
Tundra, Alpine Fields				
Conifer	18	160.2	160.2	63
Oaks	0	0	0	0
NC-NI	9	38.7	38.7	0
NC-I	9	92.7	21.60	0
LL	----	162	162	0
	180	453.6	384.3	63

2.5.3 Elements of Annual Emission Inventory

The example annual U.S. emission inventory compiled in this study is based on the following data:

1. A set of emission rates for broad categories of vegetation, leaf litter, and water surfaces. Each category has an emission factor for day, night, and winter. Since isoprene is not emitted in the dark, the difference between the day and the night emission factor is equal to the isoprene emissions. The winter emission factors assume that only conifers have emissions for winter months, and that their emissions approximate the winter emission rates of Pullman, WA conifers. All vegetation emission rates were standardized to 30°C using the terpene and isoprene emission rate algorithims shown in Figure 2-3-a.

2. The approximate areas and leaf biomass density factors for biotic regions in the U.S. were apportioned among the broad vegetation classifications, according to the abundance of each classification in each biome. Biome emission factors for each biotic region were then calculated by multiplying emission rates by leaf biomass density factors (Table 2.5-a). For "flat samples", emission factors were related directly in $\mu g/m^2 \cdot hr$. Emission factors for "marine" and "fresh water" categories were not used in this inventory. The addition of these factors would not significantly affect the inventory results.

3. Monthly minimum, maximum and average temperatures by latitudinal region were estimated for the U.S. by visually evaluating temperature isopleths. Each month was also designated as a summer or a winter month for each region based upon the temperature record. Generally if the daily minimum fell below 40°F and the average was below 50°F, the month was classified as a "winter" month. However, May was classified as a "summer" month in Region I on the basis of the solar incidence and growing season data in the Atlas.

To complete the emission inventory the biome composition of each latitudinal temperature region was estimated and hourly emission factors (in terms of terpenes and isoprene for summer and winter) were estimated for each region. Next, for each summer month the standardized emission factors were adjusted to the actual regional monthly temperature using the following scheme:

1. For isoprene emissions (only during "summer" months), the Tingey, et al., (1978a) isoprene emission rate algorithim was used to correct the emission factors from 30°C to the average monthly temperature assuming that each isoprene emission day consisted of four hours of maximum temperature and eight hours of average temperature. This daily isoprene emission rate was then multiplied by the number of days in the month.

Table 2.5-b. *AVERAGE MONTHLY U.S. TEMPERATURES BY REGION (°F)

Region	Class	Max.	Min.	Ave.
January				
I	W[1]	--	0	22
II	W	30	16	20
III	W	35	20	30
IV	W	60	40	50
February				
I	W	35	10	20
II	W	35	15	25
III	W	45	20	35
IV	S[2]	65	45	55
March				
I	W	35	20	25
II	W	45	25	35
III	W	55	30	45
IV	S	70	50	60
April				
I	W	50	30	40
II	W	55	35	45
III	S	65	40	55
IV	S	75	55	70
May				
I	S	60	40	50
II	S	70	45	60
III	S	75	55	65
IV	S	85	60	75
June				
I	S	70	50	60
II	S	80	55	65
III	S	85	60	75
IV	S	90	65	80

Region	Class	Max.	Min.	Ave.
July				
I	S	80	50	65
II	S	80	60	70
III	S	90	60	75
IV	S	90	70	80
August				
I	S	80	50	65
II	S	80	60	65
III	S	85	70	75
IV	S	95	75	80
September				
I	S	65	45	55
II	S	70	50	60
III	S	80	55	70
IV	S	85	65	80
October				
I	W	55	30	45
II	S	60	35	50
III	S	70	45	60
IV	S	90	60	70
November				
I	W	40	20	30
II	W	45	25	35
III	W	55	30	40
IV	W	70	50	60
December				
I	W	30	10	20
II	W	35	15	25
III	W	45	25	35
IV	W	65	40	50

*Estimated from A Climatic Atlas of the U.S. (U.S. Dept. Comm., 1968)

W = Winter
S = Summer

2. For terpene emissions, the terpene emission rates were corrected from 30°C to the regional monthly temperature using the Tingey, et al., (1978b) terpene emission rate algorithim. A terpene emission day was assumed to consist of four hours of maximum, 16 hours of average, and four hours of minimum temperature. The daily emission rates were then muliplied by the number of days in the month. If the month was designated as a "winter month" the winter terpene emission factor was used. Where temperatures below 25°C were encountered, it was assumed that the Tingey emission rate algorithms would still be valid.

The monthly emission estimates by latitudinal region (See Figure 2.2-a) are shown in Table 2.5-c. Annual emission estimates by region are summarized in Table 2.5-d.

From these tables it appears that natural emisions are not evenly distributed by region or by season. Approximately 43% of the total emissions occur during the summer months of June, July and August, and 45% of the annual emissions occur in the Southern United States. Of the emission in the Southern U.S., 34% is isoprene.

It is important to note that this emission inventory can only be considered a very rough estimate of U.S. biogenic emissions, for the data are too few to enable completion of a comprehensive nation wide annual inventory.

2.5.4 Limitations of Emission Estimates

There are a number of areas where more data is needed:

1. It is presently not known how the emission rate from a single tree varies over a long period. Only limited, repetitive sampling of specific trees has been done and has never continued throughout a year.

2. No samples have been collected from northern forests during the spring and summer. It is not known if summer emission estimates for northern species ever approach those of southern species.

3. The EPA-Corvallis studies were conducted over a small temperature range. Extrapolation of these emission algorithms to lower temperatures may not be valid. Emission rate algorithms probably only apply within the temperature range for which the plant was adapted. That is, cold adapted plants would probably have higher

Table 2.5-c. MONTHLY U.S. EMISSION INVENTORY (metric tons/mo) by REGION*

		Isoprene	Terpenes	Total			Isoprene	Terpenes	Total
Jan.	I	0	3.7×10^4	3.7×10^4	Feb	I	0	4.9×10^4	4.9×10^4
	II	0	8.1×10^4	8.1×10^4		II	0	1.2×10^5	1.2×10^5
	III	0	1.0×10^5	1.0×10^5		III	0	1.1×10^5	1.1×10^5
	IV	0	1.3×10^5	1.3×10^5		IV	0	1.5×10^5	1.5×10^5
Total		0	3.5×10^5	3.5×10^5	Total		0	4.3×10^5	4.3×10^5
Mar	I	0	6.8×10^4	6.8×10^4	Apr	I	0	1.2×10^5	1.2×10^5
	II	0	1.4×10^5	1.4×10^5		II	0	2.1×10^5	2.1×10^5
	III	0	1.9×10^5	1.9×10^5		III	4.5×10^3	1.2×10^6	1.2×10^6
	IV	2.2×10^5	4.6×10^5	6.8×10^5		IV	4.3×10^5	1.6×10^6	2.0×10^6
Total		2.2×10^5	8.6×10^5	10.8×10^5	Total		4.3×10^5	3.1×10^6	3.5×10^6
May	I	1.3×10^4	5.6×10^5	5.7×10^5	June	I	2.4×10^4	7.9×10^5	8.1×10^5
	II	8.1×10^4	1.3×10^6	1.4×10^6		II	2.0×10^5	1.7×10^6	1.9×10^6
	III	3.3×10^5	$1.9 \times 10_6$	2.3×10^6		III	6.9×10^5	2.8×10^6	3.5×10^6
	IV	1.1×10^6	2.1×10^6	3.2×10^6		IV	1.8×10^6	2.5×10^6	4.3×10^6
Total		1.5×10^6	5.9×10^6	7.4×10^6	Total		2.7×10^6	7.8×10^6	1.1×10^7
July	I	6.0×10^4	1.1×10^6	1.1×10^5	Aug	I	6.0×10^4	1.0×10^6	1.1×10^6
	II	3.5×10^5	2.1×10^6	2.4×10^6		II	2.0×10^5	1.8×10^6	2.0×10^6
	III	1.4×10^6	3.0×10^6	4.4×10^6		III	9.9×10^5	3.0×10^6	4.0×10^6
	IV	1.9×10^6	5.2×10^6	7.1×10^6		IV	2.4×10^6	2.8×10^6	5.2×10^6
Total		3.7×10^6	1.1×10^7	1.5×10^7	Total		3.7×10^6	8.6×10^6	1.2×10^7
Sept	I	1.7×10^4	6.5×10^5	6.7×10^5	Oct	I	1.1×10^4	1.4×10^5	1.5×10^5
	II	5.0×10^4	9.0×10^5	9.5×10^5		II	4.4×10^4	8.8×10^5	9.2×10^5
	III	5.4×10^5	2.3×10^6	2.8×10^6		III	2.0×10^5	1.6×10^6	1.8×10^6
	IV	1.4×10^6	2.4×10^6	3.8×10^6		IV	6.7×10^5	1.7×10^6	2.4×10^6
Total		2.0×10^6	6.3×10^6	8.3×10^6			9.3×10^5	4.3×10^6	5.2×10^6
Nov	I	0	7.8×10^4	7.8×10^4	Dec	I	0	5.1×10^4	5.1×10^4
	II	0	1.4×10^4	1.4×10^4		II	0	1.4×10^5	1.4×10^5
	III	0	1.5×10^5	1.5×10^5		III	0	1.2×10^5	1.2×10^5
	IV	0	1.4×10^5	1.4×10^5		IV	0	1.4×10^5	1.4×10^5
Total		0	3.8×10^5	3.8×10^5	Total		0	4.5×10^5	4.5×10^5
		Annual Total	1.5×10^7	1.5×10^7			6.5×10^7 (7.2×10^7 short tons)		

*Regions outlined in Figure 2.2-9.

Table 2.5-d. ANNUAL U.S. EMISSION INVENTORY BY LATITUDINAL REGION*
(Metric Tons)

	Isoprene	Terpene	Total
I	1.9×10^5	4.5×10^6	4.8×10^6
II	9.3×10^5	9.4×10^6	1.0×10^7
III	4.2×10^6	1.7×10^7	2.1×10^7
IV	9.9×10^6	1.9×10^7	2.9×10^7
Annual Total	1.5×10^7	5.0×10^7	6.5×10^7
	**1.7×10^7	**5.5×10^7	**7.2×10^7

* Region oulined in Figure 2.2-a.

** Short tons = metric tons x 1.102

emission rates at lower temperatures than predicted by the algorithms for Florida species.

4. More sampling should be completed to determine the emission rate variability with vertical profile for a single tree. Present emission estimates are based upon extrapolation of emission estimates from branches.

5. Emission estimates for deciduous species were assumed to be zero during winter months. Sampling should be done to confirm this.

6. Sample programs should be conducted throughout the country to see if emission estimates corroborate those reported here.

7. The relationship between leaf temperature, bag temperature and ambient air temperature and emission rates should be investigated further. For this inventory it was assumed that the emission rate as measured at a specific bag air temperature was equal to the emission rate at an equivalent air temperature and that bag air temperature was equal to leaf temperature.

8. The leaf biomass data used in this report is very generalized. More specific data about leaf biomass composition, temporal leaf biomass fluctuation due to annual climate variables such as drought or flood and the variation in leaf biomass throughout the season for each vegetation type are needed.

2.5.5 Summary of Inventory Procedure

Because of limitation noted above, the emission inventory reported here can only be considered as a "first cut" approximation of actual biogenic emissions in the U.S. However, the procedure illustrated by this inventory could be applied to smaller areas where more specific data could be determined. For this reason it is useful to summarize the inventory procedure used:

1. The U.S. was divided into biotic regions.

2. The total leaf biomass for each biotic region was estimated.

3. The compostion of each biotic region, in terms of leaf biomass for each of the emission rate categories of Table 2.4-d, was estimated. The results are emission rates for the major biotic regions of the U.S. in terms of μg emission/$m^2 \cdot hr$ (Table 2.5-a).

4. The U.S. was divided into latitudinal regions as follows: Region I = 45° - 50°; Region II = 40°- 45°; Region III = 35°- 40°; Region IV = 25° - 35°.

5. The average, the minimum, and the maximum latitudinal temperatures were estimated by month for each latitudinal region. The month was then classified as a winter or a summer month (Table 2.5-b).

6. The area of each latitudinal region and its respective biome composition was estimated.

7. The hourly emission rates for each biome were converted into monthly emission rates and into emission rates by latitudinal region using the appropriate emission rate algorithms for isoprene and terpenes.

8. For isoprene emissions, each day was assumed to consist of four hours maximum, and eight hours of average temperature for each summer month.

9. For non-isoprene emissions, each day was assumed to consist of four hours of maximum, four hours of minimum, and 16 hours of average temperature.

If a detailed inventory were desired for a specific area, similar steps would be taken:

1. Determine the major vegetation types and quantify the leaf biomass for each.

2. Develop a temperature and light regime which would describe the variability in emission rates with sufficient detail for the time period of interest.

3. Develop species specific emission factors based upon field sampling or use the broad vegetation emission factors given in Table 2.4-e.

4. Standardize the vegetation emission rates with respect to temperature, light and species composition and multiply the emission rates by their respective leaf biomass factors. Add the soil-leaf litter and water surface emission factors to the vegetation emission factors. The sum of the components is equal to an hourly emission factor for the entire area.

5. Modify the hourly area emission factor using the appropriate time scale for temperature and light conditions to arrive at total daily, seasonal or annual actual VOC emission.

2.6. Comparison With Other Biogenic Emission Estimates

Tingey et. al. (1978 a,b) reported an average emission rate from Slash Pine of 9.38 μg carbon/g·hr (10.63 μg compound/g·hr) at a leaf

temperature of 35°C. Their reported isoprene emission rates for live oak reached a maximum of 120 µg carbon/g dry weight at a leaf temperature of 44°C (136 µg compound/g·hr). At a leaf temperature of 30°C and saturating light the predicted emission rates ranged from 28.35 to 46.1 µg/g·hr. (32.14 to 52.27 µg/ compound/g·hr). These laboratory results obtained under laboratory conditions are fairly close to the emission rates of 8.9 µg/g·hr for conifers and 24.7 µg/g·hr for oaks reported in Table 2.4-e of this report. It should be expected that laboratory studies might yield slightly higher emission rates since the plants are grown under ideal conditions.

Arnts, et. al., described a micrometeorological technique to estimate the emission flux of α-pinene over an even aged loblolly pine plantation. These estimates were made by comparing vertical profile measurements of α-pinene with net radiation and vertical gradients of water vapor using an energy balance approach. Their flux estimates ranged from 13 to 119 $\mu g/m^2\ min^{-1}$ with a mean value of 52.8 $\mu g/m^2 min^{-1}$ at an average temperature of 29.7°C (Arnts, et al., 1978).

If the leaf biomass for the loblolly pine plantation is 750 g/m^2 (Arnts personal communication), then this results in an emission rate of from 1.0 to 9.5 µg/g·hr of α-pinene. If α-pinene is roughly 35% of the non-methane VOC (Table 2.4-b), then these figures are equal to an emission rate range of 1.7 to 16 µg/g·hr with an average emission rate of 6.9 µg/g·hr for loblolly pine.

The results of the studies by Tingey, et. al., and Arnts, et. al., suggest a good agreement betwen different sampling, methodologies, analytical techniques and vegetation species and also corroborate some of the emission rates used in this report.

Information available in the literature concerning the area-wide emission rates of natural hydrocarbons is very scarce. Most estimations have been based upon early work by Went (1960) and Rasmussen and Went (1965). Westberg (1977) points out that these previous emission rates are inadequate for they deal only with terpenes and their derivatives. Also, in general, it is difficult to extrapolate to national or regional biogenic emission rates from these worldwide estimates.

In order to compare the average yearly U.S. emission rate calculated in this study to the previous worldwide emissions rates, a common basis had to be found. Numerous estimates of the net amount of carbon fixed by the terrestrial vegetation of the world (net primary productivity) have been made in the course of IBP studies. These estimates, included in the The Primary Productivity of the Biosphere (Lieth and Whittaker, 1976) are based upon computer modeling maps which relate the Net Primary Productivity (NPP), measured at different points around the world, to climatological factors. The relationship between NNP and climate is then used to construct NPP isopleths. The areas of the isopleths drawn on computer generated maps can then be summed to give regional or worldwide estimates of NPP. If NPP is related to the average VOC emission rate for the U.S., and this factor (the ratio of the weight of emissions to the weight of carbon fixed) is assumed to be representative of the worldwide emission rate/NPP ratio, the annual worldwide hydrocarbon burden can be estimated. Using these assumptions an estimated total non-methane VOC emission of 8.3 x 10^8 MT/yr can be calculated based upon an ER/NPP ratio for the U.S. of approximately 0.7%. This annual worldwide estimate is roughly 10 times Rasmussen's and Went's previous estimates which included terpene compounds only, and is near the lower limit of the 1974 RTI estimate (Table 2.6-a).

Table 2.6-a. ESTIMATES OF WORLDWIDE EMISSIONS OF NATURAL VOC *

Investigator	Method	Emission Rate (tons/yr)
Went (1960)	Sum of sagebrush emission and terpenes as percentage of plant tissues	1.75×10^{8a}
Rasmussen & Went (1965)	Direct in situ ambient conc.	4.32×10^{8a}
Ripperton, White & Jeffries (1967)	Reaction Rae O_3/pinene	2 to 10 x previous estimates[a]
Robinson & Robbins (1968)	Based largely on Rasmussen and Went's data	4.80×10^{8b}
RTI (1974)	Lower limit = 10 x Rasmussen and Went's figure Upper limit = .10 x total carbon fixed by green plants	$0.4 - 1.2 \times 10^{10b}$
Zimmerman (1978)[c]	$\frac{\text{Annual US Natural Emissions}}{\text{Annual US NPP}} \times \text{World NPP}$	8.3×10^{8}

*Adapted from Westberg 1977

[a]Biogenic hydrocarbn emissions, i.e. terpenoid vapors

[b]Biogenic organic emissions

[c]This study (extraplating nationwide estimated to the world)

REFERENCES

Alexander, J. T., "Emission Inventory of Petroleum Storage and Handling Losses" in: Emission Inventory/Factor Workshop, Vol II. EPA Office of Air Quality Planning and Standards, 1977.

American Association for the Advancement of Science, Primary Productivity and Mineral Cycling In Natural Ecosystems. A Symposium. 13th Annual Meeting, New York City, December 27, 1967.

Arnts, R. R., Seila, R. L., Kuntz, R. L., Mowry, F. L., Knoerr, K. R. and Dudgeon, A. C., "Measurements of α-Pinene Fluxes from a Loblolly Pine Forest." Fourth Joint Conference on Sensing of Environmental Pollutants, American Chemical Society, Washington, D.C., pp. 829-833, March 1978.

Dasmann, R. F., Environmental Conservation (4th Ed.), Int. Union for the Conservation of Nature and Natural Resources, Morges, Switzerland. 1976.

Duce, R. A., "Speculations on the Budget of Particulate and Vapor Phase Non-Methane Organic Carbon in the Global Troposphere," Phageoph, Vol. 116, 1978.

Gates, D. M., "Heat Transfer in Plants," Sci. Am. 213:76-84, 1965.

Holdren, M., "Letter Report to Members of the CRC-APRAC, CAPA-II Project Group," October 17, 1978.

Kamiyama, K., T. Takai, and Y. Yamanaka, "Correlation Between Volatile Substances Released from Plants and Meteorological Conditions" in: Proceedings of the International Clean Air Conference, Brisbane Australia, 1978.

Lieth, H., and R. H. Whittaker, (eds.), Primary Productivity of the Biosphere, Springer-Verlag, New York, 1975.

Miller, P. R., and R. M. Yoshiyama, "Self Ventilated Chambers for Identification of Oxidant Damage to Vegetation at Remote Sites." Environmental Science and Technology, 62490, Kb 10, Jan. 1973.

National Academy of Science, Productivity of World Ecosystems. Proceedings of a Symposium presented Aug. 31 - Sept. 1, 1972 in Seattle, WA. Wash. D.C., 1975.

Rasmussen, R. A., "Isoprene: Identified as a Forest-Type Emission to the Atmosphere." ES & T, Vol. 4, 8, pp. 667-671, 1970.

Rasmussen, R. A., and Went, F. W., "Volatile Organic Material of Plant Origin in the Atmosphere," Proc. N.A.S., vol. 53, pp. 215-220, 1965.

Rasmussen, R. A., "What do the Hydrocarbons from Trees Contribute to Air Pollution?", J. of Air Pollution Control Association, Vol. 22, No. 7, pp. 537-543, 1972.

Research Triangle Institute, "Natural Emissions of Gaseous Organic Compounds and Oxides of Nitrogen in Ohio and Surrounding States," Final Report, EPA Contract 68-02-1096, 1974.

Ripperton, L. A., White, O., and Jefferies, H. E., "Gas Phase Ozone-Pinene Reactions," Div. of Water, Air, and Waste Chemistry, 147th National Meeting American Chemical Society, Chicago, IL., pp. 54-56, September, 1967.

Robinson, E., and R. C. Robbins, "Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants," SRI Final Report, PR-6756, 1968.

Rodin, L. E., N. I. Bazilevich, N. N. Rozov, "Productivity of the Worlds Main Ecosystems," in: Productivity of World Ecosystems, N.A.S., 1975.

Sanadze, G. A., Kalandadze, A. N., "Light and Temperature Curves of the Evolution of C_5H_8," Fiziologiya Rastenii, Vol. 13, No. 3, ppb 458-461, May - June, 1966.

Sanadze, G. A., "Absorbion of Molecular Hydrogen by Illuminated Leaves," Fiziologiya Rastenii, Vol. 8, No. 5, pp. 555-559, 1961.

Satoo, T., "Primary Production Relations in Woodlands of Pinus Densiflora," in: Primary Productivity and Mineral Cycling in Terrestrial Ecosystems. Symposium, Ecological Society of America, American Association for the Advancement of Science, 13th Annual Meeting, Dec. 27, 1967, New York City.

Tingey, D. T., H. C. Ratsch, M. Manning, L. C. Grothaus, W. F. Burns, and E. W. Peterson, "Isoprene Emission Rates from Live Oak," Final Report, EPA CERL-040, May, 1978.

Tingey, D. T., M. Manning, H. C. Ratsch, W. F. Burns, L. C. Grothaus, and R. W. Field, "Monoterpene Emission Rates from Slash Pine," Final Report, EPA CERL-045, August, 1978.

U.S. Dept. of Commerce: A Climatic Atlas of the U.S., 1968.

Went, F. W., "Blue Haze in the Atmosphere," Nature, pp. 641-643, August, 1960.

Westberg, H. H., "The Issue of Natural Organic Emission" in: International Conference on Oxidants 1976 Analysis of Evidence and Viewpoints, EPA-600/3-77-116, October 1977.

APPENDIX A

EXPERIMENTAL VERIFICATION OF SAMPLE METHODOLOGY

A.1. INTRODUCTION

This appendix is intended to explain the rationale for the development of the sampling methodology outlined in the main report. It details the evolution of the field testing methodology and includes experimental verification procedures, and "dead ends." It is designed to aid researchers who wish to refine the sampling or analytical techniques used in this study. The explanation of WSU's technique development should also minimize experimental back-tracking.

A.2. PROJECT OBJECTIVES

The objectives of this study were as follows:

1. To develop a standardized sampling and analytical methodology
2. To develop emission factors for a limited number of species
3. To develop standardized emission inventory techniques
4. To develop an example nation wide emission inventory of biogenic emissions

A standardized sampling and analytical methodology was desired so that emission estimates could be easily generated by different laboratories and could be directly compared. Thus, the techniques developed were to be fairly simple and were to use non-specialized, commercially available equipment where possible. It was desirable that the experimental procedures allow for alternate funding levels and equipment availability which might occur among laboratories.

The development of emission factors for a limited number of vegetation species, leaf litter and water surfaces was meant to serve the dual purposes of testing the methodology and of generating a data base which could be used in preliminary emission inventories. The data generated would also provide a historical comparison for past and future emission rate data.

The emission factors developed were to be applied to standardized emission inventory procedures. A nationwide emission inventory using the

standardized methodology would then serve to demonstrate the procedures involved. Thus a nationwide inventory was to be developed in a format so that the data could be easily applied as a preliminary estimate for a specific area, or could be easily refined as additional locale-specific data was generated.

A.3. SAMPLING APPROACHES

There are a number of possible sampling approaches which might be applied to fulfill the project objective. The following were considered to be the most likely alternatives for this project:

A.3.1. UPWIND/DOWNWIND OR VERTICAL GRADIENT SAMPLING

The upwind/downwind method involves the collection of a sample upwind of the vegetative area of interest and simultaneously collecting a sample downwind of the area. The difference in total non-methane organic emissions between the two samples is then assumed to be due to the vegetation effects. If desirable, the biomass unit of interest (leaf, twig, leaf and branch; or surface area) for the vegetation stand can be calculated and an emission rate can be estimated.

The upwind/downwind procedure requires a very carefully selected site. The air entering the vegetation must be relatively clean. It is also important that the incoming air be uniform with respect to composition and concentration.

The advantages of this sampling methodology are that the sampling procedure itself is "outside the system" and thus does not affect emission rates. Ths methodology also results in a net emission flux from the vegetation, so sources, as well as sinks, are automatically included.

The upwind/downwind approach has several profound disadvantages. First, the logistics of operating two simultaneous sampling sites presents

problems. These problems include sample timing, instrument calibration, personnel limitations and site selection.

Secondly, it is nearly impossible to find an ideal site. Most sites represent compromises in that they are affected by the wind shifts due to local terrain effects or weather patterns, mixing of the incoming air, and the vegetation emissions are never uniform. Moreover, anthropogenic emissions invariably impact on the vegetation study area. The end result is that a large number of samples are required so that trends can be determined. This procedure has the additional disadvantage in that biogenic hydrocarbon emissions reacting between the sampling points are not accounted for. The upwind/downwind scheme, therefore, invariably requires complicated and highly speculative modeling to estimate emission rates. Additionally, rural ambient VOC levels are usually quite low and, therefore, problems of analysis and accurate quantitation are extensive. Also these programs are very expensive by nature. Finally, the upwind/downwind approach can not readily isolate any of the variables which might affect emission rates. These variables include heat, light, and relative humidity.

The vertical gradient approach, such as that used by Arnts, et al., (1978), which attempts to establish a vertical profile of selected hydrocarbons within a forested canopy, is essentially a variation of the upwind/downwind approach and shares similar advantages and disadvantages.

A.3.2 ENCLOSURE SAMPLING

An alternative to upwind/downwind and vertical gradient sampling is enclosure sampling. The basic method involves placement of an enclosure chamber around the selected vegetation to isolate it from some of the variables of the surrounding environment.

This technique has several inherent advantages:

1. Higher concentrations of emissions can usually be obtained, which allows one to use simpler and more accurate analytical techiques.
2. No model is needed to determine source strengths. Source emissions are directly measured.
3. Better control can be attained over variables which might affect emission rates. If these variables are better known it is easier to accurately extrapolate emission rates spatially and temporally.
4. The sample site selection is not so critical. Usually this approach allows emission testing even in areas of high anthropogenic concentrations.
5. As a result of the above advantages, the sampling programs tend to be less expensive and more portable.

There are a number of enclosure techniques which have been used previously for vegetation emission/uptake studies and were considered for use in this project.

A.3.2.1 Regulated Enclosures

The most sophisticated type of enclosures can be classified as regulated enclosures. This type of enclosure has often been used to evaluate seasonal fluctuations of CO_2 emissions from a specific portion of a branch. The regulated chambers provide control of temperature, relative humidity, and often even light. They are designed to maintain long-term environmental equilibrium and control over the portion of vegetation or whole plant of interest. This type of chamber has inherent disadvantages for use in the measurement of hydrocarbon emissions from vegetation:

1. The most common materials of construction include plexiglass, neoprene gaskets, and other components which may emit VOC.

2. Long-term equilibrium invariably requires the circulation of air through a conditoning system which cools and controls the humdity of the environment. VOC emissions could conceivably be lost in such a system. An experiment conducted in our laboratory to try to remove some of the moisture from an air sample illustrated this point. When the sample was passed through a 3 foot length of coiled 1/16 inch (o.d.) stainless-steel tubing cooled to 0°C or lower, all of the hydrocarbons above C_2 were lost.

3. Regulated enclosures are usually meant to be semi-permanent, therefore, a wide variety of species could not be sampled in an emission inventory program.

4. These enclosures require external 110-120 volt power or elaborate battery systems which limit their portability and also put a constraint on possible sample sites.

A.3.2.2. Compensated Chambers

Compensated chambers are a class of enclosures which attempt to compensate for the inescapable enclosure effects of temperature and moisture buildup. The open-top chambers used for the study of ambient pollutant effects on vegetation are an example. This type of chamber is often quite large and encloses a whole tree. It relies upon a fast exchange rate (up to eight exchanges per minute) of the air inside the chamber to minimize heat and metabolic by-product buildup. Usually the chamber has a filter on the inlet and a collecting device on the outlet. Often the tops of the chambers are painted white to minimize heating. They are usually provided with self ventilating wind powered stacks to enhance air flow and to minimize the need for electric power. However, the temperature within the chamber may reach temperatures above 44°C (6°C above ambient air temperature) even at an air exchange rate of 3.5 times per minute (Miller and Yoshiyama, 1973).

The disadvantages of these types of chambers for the measurement of VOC emissions from vegetation include:

1. The high flow rates required result in low sample concentrations which, in turn, necessitate a high degree of analytical sensitivity.

2. The filtering and sample collection techniques required would be quite complicated if it was desirable to quantify the full range of organic emissions.

3. Compensated chambers typically are semi-portable at best and are meant for long-term installation.

4. The cost of this type of approach would be very high for a widespread, short-term project.

A.3.2.3 Static Chambers

The simplest and least expensive enclosure approach is the static chamber approach such as that used by Rasmussen (1972) and Sanadze (1961). In this method a portion of vegetation is enclosed for a specified length of time and a sample is collected from the chamber.

This method has the advantages of being relatively inexpensive and portable. In addition, high VOC levels can be generated that enhance analysis and quantitation.

The static chamber method has the following disadvantages:

1. There is no control over the buildup of heat, water vapor, CO_2 or other metabolic products, which can affect emission rates.

2. If the enclosure is rigid, anthropogenic VOC emissions will "invade" the chamber as the sample is withdrawn. Also, the chamber is full of ambient air at the time of enclosure. If anthropogenic VOC emissions are high they may obscure vegetation emissions.

A.3.2.4 WSU Static/Dynamic Enclosure

After evaluation of the preceeding techniques and preliminary collection of samples using the static system, a static dynamic sampling procedure was developed. Basically, the method which evolved involves enclosing a portion of the vegetation of interest with a Teflon bag, sucking most of

the ambient air out of the bag and thus collapsing the bag around the branch, and collecting a sample of the air from the collapsed bag. The bag is then quickly filled with a known volume of air which is free of all VOC and has a controlled level of CO_2. After the bag is partially inflated, another sample is collected while zero air continues to flow into the enclosure at a rate slightly higher than the sample rate. The difference between the hydrocarbon content of the bag, divided by the time interval between the two samples, is the emission rate of the vegetation. This emission rate can then be divided by a foliage unit such as biomass or surface area to result in an emission rate per unit vegetation per unit time. Total enclosure time is on the order of 15 minutes. The method has several advantages:

1. The short enclosure time and large volume of zero-air minimizes heat buildup and water vapor accumulation, which ensures that the emission rates are not disturbed.

2. The ultraclean air entering the enclosure and the organic emission concentrations which accumulate in the zero air enhance analytical sensitivity and precision.

3. The equipment is fully portable. A wide variety of emission samples can be collected in a relatively short field sampling period.

4. Emission samples can be collected practically anywhere, the procedure is not site-selective since anthropogenic contributions are minimized.

The method requires the following resources:

1. An enclosure which does not contribute to or "scrub" hydrocarbon emissions.

2. A source of clean "zero air"

3. A method to take a sample from the enclosure and transport it to the laboratory for analysis while preserving its integrity.

The static/dynamic approach has disadvantages in that:

1. A portable source of clean "zero air" may not be readily available.

2. Each major vegetation-type must be sampled (a disadvantage common among all enclosure techniques).

3. There is a possible disturbance of the vegetation emission due to the sample collection procedure. This disadvantage is also common among any methodology which does not remain "outside the system".

A.4. ZERO AIR

The sampling methodology is dependent upon source of clean "zero" air. The air is required to be uniform in composition and preferably should have a total VOC concentration of 10 $\mu g/m^3$ or less. Sources of zero air which have high levels of hydrocarbons could be used; however, care must be taken to "fingerprint" this air source so that amounts and species of hydrocarbons present can be quantitated and subtracted from emission rate values. This adds to the expense and complexity of performing all analyses. During the developement of the sampling procedure, WSU evaluated a number of possible zero air sources. These included commercial zero grade air from Matheson and Scott, molecular sieve filters, hydrocarbon combusters, and two commercial brands of zero air generators: The Meloy pure air source and Aadco zero air source.

A.4.1 COMMERCIAL ZERO AIR

Our evaluations revealed that N_2 and O_2 levels in commercially available cylinders were not uniform from cylinder to cylinder. It is not known what effect this might have on vegetative emission rates, however it was felt that an air supply of uniform composition would help to limit some of the variables which might affect emission rates. Also, most tanks had variable levels of methane and various higher hydrocarbons.

A.4.2 MOLECULAR SIEVE FILTERS

Molecular sieve filters work well in removing most higher hydrocarbons above C_2; however, breakthrough of the C_2 hydrocarbons can occur quite rapidly.

A.4.3 HYDROCARBON COMBUSTER

The hydrocarbon combuster consists of a platimum wire coil in a glass tube. The wire is heated until it is red hot and the air to be cleaned has passed over it. The hydrocarbon combuster could only process air at the rate of 1 liter/minute. However the outlet air was hydrocarbon free. The construction of the combuster did not allow pressures to exceed 5 psig. The outlet also had variable CO_2 and moisture levels.

A.4.4 MELOY PURE AIR SOURCE

The Meloy pure air source is essentially a series of molecular sieve filters. In operation, one filter is on-line and a portion of its filtered outlet air is used to back-flush the other filter. Periodically the flow through the filters is switched so that a clean filter is always on line. The Meloy we tested allowed passage of light (C_2) hydrocarbons. Also, the materials of construction emitted hydrocarbons, and concentrations less than 1 ppmC could not be obtained.

A.4.5 AADCO PURE AIR GENERATOR

The other commercially available unit, the Aadco pure air generator, also uses switching molecular sieve filter units. However, it uses a very short cycle time (30 sec) and two sets of molecular sieve filters. After passing through the molecular sieve filters, the outlet air enters a catalytic combuster which is maintained at $\sim$400°C and eliminates methane and

C_2 hydrocarbons which may pass through the molecular sieve filters before back-flushing. The unit can supply pressures up to 80 psig at a rate of up to 10 liters/minute. The air leaving the combuster can be routed through a Mallcosorb® (indicating Ascarite) scrubber to eliminate CO_2. The result is air which has the the same N_2/O_2 ratio as ambient air and a dew point of minus 60°F. WSU has concentrated up to 10 liters of this zero air using the freeze-out loop method (previously described as a sample concentration step prior to analysis), and have found no hydrocarbons. WSU has also checked the output for fluorocarbons and has found none. The Aadco pure air source was thus selected for use on the project and has been used continually throughout the year. It has been found to be a reliable source of zero air.

A.4.6 CRYGENIC COMPRESSION OF ZERO AIR

Since the zero air generator required an external source of 110 volt power, WSU had to develop a method to get large quantities of zero air into the field. The method developed consists of immersing tne base of a clean, empty medical grade oxygen cylinder in liquid nitrogen and connecting the valve opening to the outlet of the zero-air source. Air is cooled as it enters the cylinder and is condensed. The inlet flow rate and the cylinder capacity are known. Enough air is placed in the cylinder so that when the cylinder is removed from the liquid nitrogen and equilibrated to ambient temperature, the cylinder is filled to approximately one half of its rated capacity. Typically, cylinders are used that are rated at 1800 - 2000 psig and which have been burst checked to 6000 psig. WSU then cryogenically compresses approximately 900 psig of zero air in them. Medical grade oxygen cylinders are used because they are required to be oil-free and therefore, usually require no cleaning. The cryogenic compressing procedure should be

used only under close supervision of trained personnel using the proper safety equipment and precautions. Alternatives to the cryogenic compression method are to put the zero air for use in the emission sampling procedure into large clean Teflon bags, or to compress the zero air output directly into large low-pressure (80 psia) tanks.

A.5 SAMPLE METHODOLOGY CHECKS

It is important that the procedure used for sampling emissions minimizes the disturbance of the enclosed vegetation. To insure that the procedure meets with this criterion, the CO_2 content of the bag as well as its temperature are routinely monitored. Periodic tests are also made to monitor the relative humidity of the bag. WSU has found that if the bag is in direct sunlight on a cool day (e.g. 10°C), the bag temperatures might be up to 10°C warmer than ambient temperatures. Also, the bag air tends to heat up rapidly if the transpiration rate of the enclosed vegetation is low. For most samples collected to date, the enclosure temperature is usually the same as the ambient temperature.

A.5.1. RELATIVE HUMIDITY

The zero air used in the procedure is dry (i.e., the dew point is -65°C). However, we have monitored the relative humidity in the enclosure and have found that it rapidly reaches a relative humidity very close to that of ambient air at the time that the emission sample is collected. If desired, the relative humidity of the incoming air could be adjusted by use of a bubbler system to approximate the moisture content of ambient air.

A.5.2 CO_2

CO_2 concentrations in the bag in sunlight were also periodically monitored. WSU found that the levels of CO_2 in the bag in sunlight were lower

than typical levels in ambient air by 5 to 10 percent. For some samples that were collected in the dark, CO_2-free zero air was used. Under these conditions, CO_2 levels in the sample were approximately equal to or slightly higher than those of ambient air at the time of sampling. No changes in emission rates with CO_2 concentration have been detected to date.

Finally, WSU's sampling procedure has been evaluated by a plant pathologist and a plant physiologist (personal communication with Dr. M. Pack, plant physiologist, WSU, Air Pollution and Resources, and Dr. R. Rasmussen, Professor Environmental Technology, Oregon Graduate Center, respectively.) They feel that due to the very short enclosure time (15 min.), the sampling procedure should not significantly affect the vegetation emission rates.

A.5.3. SAMPLE INTEGRITY

Sample integrity in the stainless steel sampling canisters has been checked by placing known standards in the cans and periodically analyzing the contents. WSU has also collected vegetation emissions in a stainless steel canister and periodically analysed its contents. The results confirm that measureable amounts of hydrocarbons are not lost on the container walls between the time of sampling and analyses. Repeated analyses over a time period of one week do show some shift in the component peak concentrations of the sample for some canisters; however, the total non-methane organic carbon content of the cans tested has remained stable to within 15% over a one-week time period. Usually samples were analysed within 24 hours of sample collection.

A.6. ANALYTICAL METHODOLOGY CHECKS

A.6.1. SAMPLE ENRICHMENT

The sample enrichment procedure is explained thoroughly in the main report. It is a procedure which has been duplicated in many laboratories. It involves slowly putting a sample through a 1/8" stainless steel loop that is filled with glass beads and is immersed in liquid O_2. Organics in the sample are frozen out on the glass beads. WSU has checked the effluent from the freeze-out loop for breakthrough of C_2-C_{12} hydrocarbons and has also compared peak heights obtained by directly injecting a quantitative standard. WSU has then made dilutions of this standard and frozen out an equivalent amount using the freeze-out technique. The results are identical.

A.6.2. HYDROCARBON ANALYSIS

Columns and conditions are explained in the instruction manual. We used neohexane as a quantitative standard. Qualitative standards were prepared and the tentative identification of sample components was made on the basis of retention time. The identification of the emissions was confirmed using a G.C. Mass Spectrometer system. The G.C. Mass Spectrometer also provided an independent means of comparing the quantitation of samples analysed via FID. The results were in good agreement.

A.6.2.1 Oxygenates

WSU conducted an experiment to determine the possibilty that oxygenates may be lost in the sample train between sampling and analysis. For these experiments a closed 1m x 1.5m Teflon bag equipped with Teflon-brass fittings and a Teflon-backed Silicon-rubber septum was used. The bag had a capacity of approximately 400 ℓ. Three hundred liters of zero air was placed in the bag and 1 to 2 μl (liquid) each of propionaldehyde, butyraldehyde, crontonadldehyde, valeradehyde, iso-valeraldehyde and benzaldehyde was injected via a micro liter syringe through the septum. These aldehydes were chosen because they were readily available and were thought to be representitive of some of the oxygenated species which might be emitted from vegetation. Another 50 liters of zero air was then added to facilitate mixing. Concentrations ranged from 0.5 to 2 ppm (v/v) compared for each component. The field sampling train (pump, tubing, portable sampling manifold) was then connected to a bag fitting and a stainless steel canister was filled. Samples were transferred from the bag through the sample manifold into the canister using Teflon tubing and copper tubing. The Teflon bag was connected directly to the G.C. sample loop and sampled. The G.C. sample loop was also filled by connecting the bag to the loop with about 1m of 1/8" OD Teflon tubing and with 1m of 1/8" OD stainless steel tubing. The bag and its contents were stored for 24 hours and the can filling and sampling procedures were repeated.

The results indicated that on the first day there was an initial loss of about 30% in the sample train regardless of whether copper and Teflon sample lines were used. This could be accounted for if the bag had not equilibrated properly before sampling. The experiment was then repeated the second day after the bag contents had time to equilibrate. The

concentrations measured in the bag were 50% lower. This loss could represent better equilibration of the contents, as well as overnight storage loss in the Teflon bag. When the bag was sampled through the portable sample manifold, no significant differences in G.C. response could be noted among direct bag injection, collection of the sample through the manifold with copper tubing or with teflon tubing. When the bag contents were introduced directly into the sample loop and compared with the results obtained when the bag sample was transferred into the loop using Teflon tubing and stainless steel tubing, the G.C. response indicated a slight loss due to stainless steel tubing (α3%) and a greater loss due to the Teflon tubing (α10%).

Experiments have also been conducted by Mike Holdren (Assistant Chemist, WSU) to test the storage efficiency of the stainless steel canisters for aldehydes and ketones as part of a CRC-APRAC CAPA-11 project. These tests were accomplished by adding nanogram amounts of an aldehyde-ketone mix to canisters filled with rural ambient air. Addition of an internal standard (neohexane) provided for better quantitative analysis. It was also felt that the addition of rural air would represent the best sampling matrix for these stability tests. The construction dates of the canisters chosen for the experiment varied from four years to less than six months. During an earlier study with the compound α-pinene, it had been discovered that the age of the container could be important, i.e. accelerated loss of α-pinene tended to occur in the older canisters.

During the three-week test period gas chromatographic analyses were completed on the canisters. Table A.6.2-a indicates that the majority of the compounds remained within 15% of the original concentration level (10-20 ppb). However, in two of the newer containers there were losses of furfural

Table A.6.2-a. LONG-TERM STORAGE OF ALDEHYDES AND KETONES IN STAINLESS STEEL CANISTERS**

	% Change Over Three-Week Period		
Compound	Can 1	Can 2	Can 3
Acetone	+10%	+13%	+12%
Neohexane	0%	0%	0%
Butyraldehyde	- 7%	-17%	-27%
Methyl-ethyl-ketone	+ 9%	-14%	-19%
Crotonaldehyde	+ 9%	- 6%	- 9%
Valeraldehyde	- 2%	-31%	-35%
Methyl-isobutyl-ketone	+10%	- 1%	+ 2%
Furfural	- 2%	-22%	-49%
2-Heptanone	+15%	-13%	- 7%
Heptaldehyde	+ 6%	-50%	-76%
Benzaldehyde	+ 6%	-14%	-13%
2-Octanone	+10%	-46%	+24%

*From Oct. 17, 1978 letter report to CRC-APRAC CAPA-II Project Group, by Mike Holdren, WSU, Air Pollution and Resources.

and heptanal. Part of these apparent losses were later thought to be due to a malfunction of the peak integration equipment. For this reason the results shown in Table A.6.2-a are "worst case".

The possibility that oxygenates may be sampled but not "seen" by the GC-FID's was examined two ways. First, a column (Durapak-low K) was made and oxygenate standards were run to determine response factors and elution times. Quantitations of oxygenates is difficult, for standards are difficult to make because they are so "sticky." Their FID response varies with each species so calibration using a representative hydrocarbon would result in inaccuracies. The G.C. Mass-Spectrometer was also used to check for the presence of aldehydes in the samples. To date no oxygenates have been detected in the emission samples analyzed via G.C. Mass-Spectrometer. At this time, however, WSU is just developing techniques to insure accurate quantitation of low levels of heavy oxygenated hydrocarbons in ambient air. These techniques are not presently routinely available to all laboratories.

A.6.2.2. Analytical Precision

The accuracy and repeatability of the analytical technique has been thoroughly tested. We have determined that the error associated with quantitation of the total hydrocarbons in a sample is a fixed amount rather than a percent of the total. This fixed error is 5 - 10 ppb and represents the error associated with the integration of very small peaks, background bleed from the column substrate and inaccuracies in sample introduction.

To determine the error in the sample introduction technique, WSU diluted a standard concentration of neohexane in a 5.5 liter stainless steel can using zero air as a diluent. Then the sample was run five consecutive times to determine the range and standard deviation. It was

subsequently determined that using the vacuum introduction system, the range was 0.08 $\mu g/m^3$ and the standard deviation was 0.04 $\mu g/m^3$. The average concentration of the neohexane standard was 1.35 $\mu g/m^3$.

4.6.2.3. Analytical Problems

Water introduced into the freezeout loop because of samples which have extremely high humidity, can cause problems when samples are analyzed using SCOT columns. The water evidently creates a stripping action on the column and results in broad extraneous peaks. A 10' (3.1m) durapak-low K precolumn was added to minimize these effects.

Water also affects the C_2 - C_6 analysis. Specifically, it causes ethylene to elute as a broad unquantifiable peak. The use of a potassium carbonate trap on the sample inlet minimizes this effect. However, if the sample is introduced into the freeze-out loop too quickly the sample may still not be dry enough. WSU, therefore, chose to duplicate the analysis for the C_2 hydrocarbons on a Porapak Q column. This column substrate is not affected by samples of high relative humidity and the analysis can be performed quickly. Comparisons of C_2 hydrocarbons from the isothermal G.C. and from the temperature-programmed light hydrocarbon G.C. was favorable for low-humidity samples.

High concentrations of CO_2 may interfere with the analysis of C_2 hydrocarbons using the Porapak Q column. This only occurred for some of the early soil plug experiments when a soil plug was left enclosed in a static chamber for a number of hours. The effect is noted as a negative peak which may interfere with ethylene quantitation.

A.7. EXPERIMENTAL DEAD ENDS

A.7.1. SOIL/LEAF LITTER SAMPLES

The first procedure used by WSU to try to estimate soil/leaf litter emissions involved cutting a plug of soil and placing it in an air tight stainless steel bucket. The bucket was taken to the lab and pressurized. A head space sample was then removed for analysis. The procedure resulted in emission rates which varied widely between samples. The enclosure time was usually 1 to 3 hours. During this time period CO_2 and water vapor accumulated in the chamber which adversely affected the analytical procedures. Next, WSU tried driving a cylinder (open on one end) into the ground 4 to 8 cm. A pump was put on the inlet side that pumped air through the cylinder into a sample collection chamber. This procedure also failed due to contamination of the sample by auto exhaust components. Also very large emission rates for forest soils were sometimes observed due to the cutting of needles and leaves along the edge of the sampler.

To alleviate the above problems, the stainless steel bucket (which had been used earlier for soil plug enclosure experiments) was inverted over the soil and its edges sealed with moist soil. The bucket was then flushed with zero air and slowly purged at a faster rate than the sample was removed. This procedure worked fairly well; however, difficulty remained in maintaining a seal around the chamber base. Also, all samples were collected in the "dark" using this method.

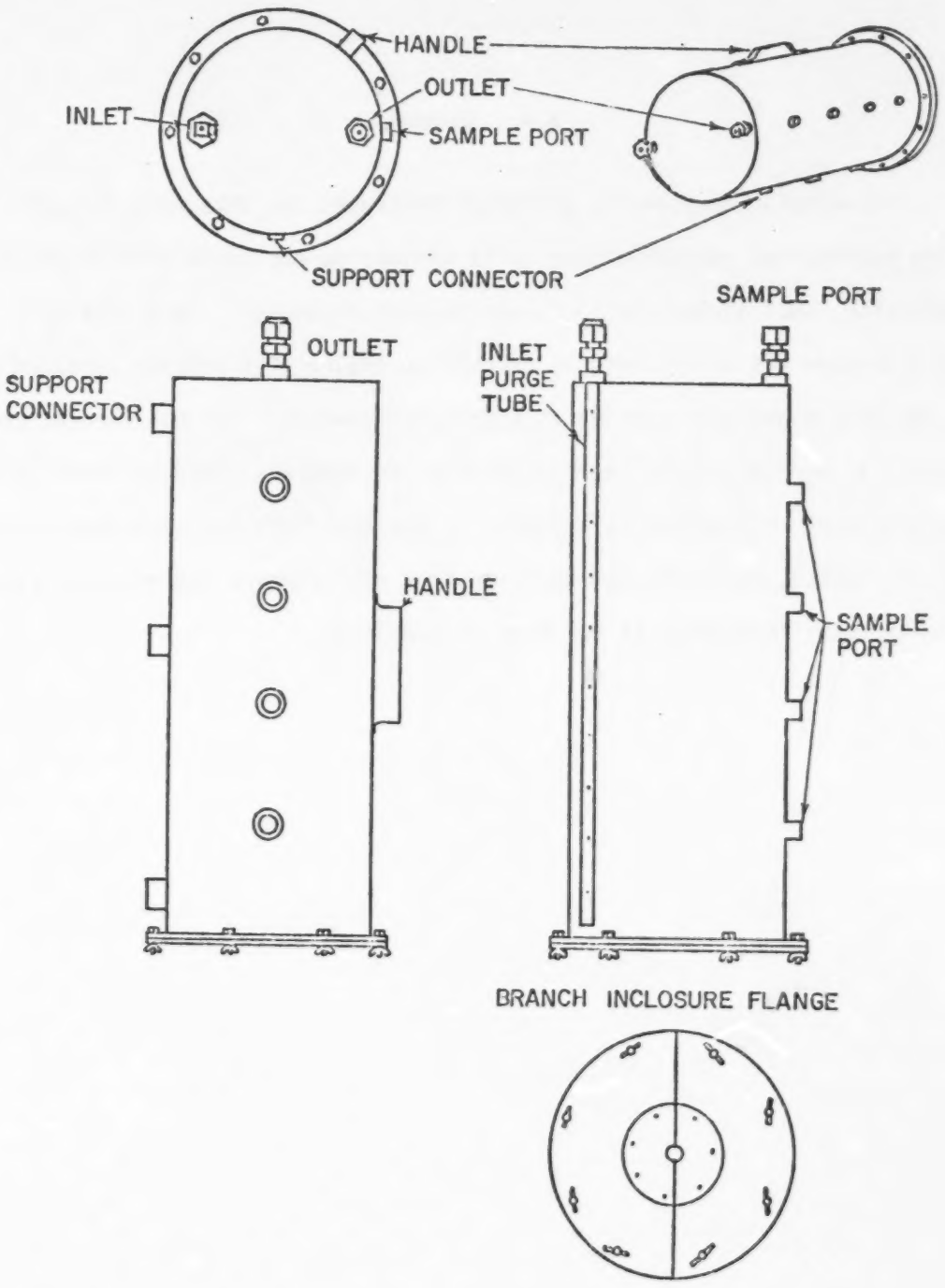
The method WSU settled upon is outlined in the main report. Basically, a soil sealing ring is driven into the ground and a concentric bag collar (which is open at both ends) is placed inside the ring. The interspace between the two rings is filled with dirt. A Teflon bag is then placed over the inner "bag collar" and the procedure used for vegetation samples is duplicated. This procedure can also be used to collect samples over ponds and marshes by inserting the bag collar in a flotation ring of closed cell polyethylene (two water-ski belts sewn together).

4.7.2. VEGETATION SAMPLES

The initial vegetation enclosure used in this study is shown in Figure A.7.2-a. It was constructed of stainless steel, measured 30 cm in diameter by 90 cm in length, and weighed about 16 kg. It had a plate at its base (the end that faced the tree trunk) which had a number of inserts with holes of different sizes to fit snugly around different sized branches. It was equipped with an inlet zero air tube with small holes along its side to promote even mixing. It also had numerous available sample ports and fittings for support brackets. This enclosure apparatus was abandoned because it was difficult to handle and did not allow samples to be taken under daytime conditions since the chamber kept out all light. WSU found that Teflon bags were easier to clean than expected, much easier to use, and allowed light to enter. Hence, Teflon was adapted for use in this study.

Figure A.6.2-a

STAINLESS STEEL SAMPLING CAN



A.8. SUMMARY

The emission measurement procedure developed for this project maximizes hydrocarbon concentrations while minimizing enclosure effects on vegetation, such as heat build-up and vegetation damage. Each step of the procedure has been carefully checked to insure that nothing is added to the sample and that nothing is subtracted from it. WSU has checked the analytical procedures for reproducibility and accuracy. WSU believes that the result of this method is a realistic emission rate for each vegetation species tested, and that each emission rate approximates the emission rate of unenclosed vegetation at the time of sampling.

APPENDIX B

DETAILED DERIVATION OF EMISSION RATE FORMULAS

B.1. INTRODUCTION

This appendix details the derivation of the emission rate formula. It also shows how to calculate emission rates for samples collected using various types of equipment and techniques.

The laboratory data format (Figure B.1-a.) lists and defines the emission variables needed and contains the information necessary for the calculation of emission rates. Depending upon the sampling procedure used, not all of the blanks will be filled. For example, if a background sample is collected and a bag blank and/or ambient air sample are not, the spaces for ambient air data and bag blank data will remain empty. Empty spaces should always be marked with a dash to indicate that the data were not collected. Questionable data should be marked with an asterisk and a note at the bottom referring to a laboratory notebook or to the field notes for a full explanation. The sample illustrated in the figure utilized a bag blank sample, an ambient air sample and an emission rate sample to determine emission rates. The sample canisters had not been evacuated prior to sampling. Instead they contained zero air at ambient pressure. This procedure was modified for later samples (background and emission sample, evacuated canisters) and the simplified emission rate formula was used. The old procedure included here as an illustration of another emission rate collection technique and calculation procedure which might be used if, for example, an evacuation system was not available.

Figure B.1-a. Laboratory data format

Date collected 9/28 Sample # 122

Date collected 9/28 Species Ponderosa Pine

		Sample	Blank
T_0 :	Time* at sample enclosure	1618	1549
T_1 :	Time at end of background sample	---	---
T_2 :	Time at start of flush	1620	1551
T_3 :	Time at end of flush	1626	1557
T_4 :	Time at start of purge	1626	1557
T_5 :	Time at start of sample collection	1627	1558
T_6 :	Time at end of sample collection	1633	1603
H_a :	(°C) Ambient Temperature at Time of Sampling		28°C (est.)
Z_f :	(ℓ/min) Zero air flush flow rate (10 ℓ/min)		10
Z_p :	(ℓ/min) Zero air purge flow rate (2 ℓ/min)		2
Ve :	(m^3) Dead volume of sample enclosure at STP (760 mm, 22/C) for bags = residual volume after enclosure, before flush.		0.025
Ve^1:	(m^3) Dead volume of enclosure bank at STP (= zero for bags)		0
Pc_s:	(psig) Pressure of sample can after sample collection		15
Pc_a:	(psig) Pressure of ambient air can after sample collection		15
Pc_e:	(psig) Pressure of enclosure blank can after sample collection		15
Pc_b:	(psig) Pressure of background can after sample collection		---
Pb :	(psia) Residual pressure of zero air in the sample cans		13.49

* Barometric pressure $\frac{\text{mm Hg}}{51.7\ \text{mm/psig}}$ for cans flushed with zero air

(ambient air can flushed, no dilution)

= Zero for fully evacuated cans

C_{ss}:	($\mu g/m^3$) TNMOC measured in vegetation sample	1248
C_{sb}:	($\mu g/m^3$) TNMOC measured in background sample	---
Cs_a:	($\mu g/m^3$) TNMOC measured in ambient air sample	137
Cs_e:	($\mu g/m^3$) TNMOC measured in enclosure blank sample	38
SA:	(cm^3 or g) Area or biomass of sample vegetation	273.95g

*Time refers to the hour and minute of the day. From this the length of enclosure time (in minutes) can be determined.

B.1.1 DEFINITION OF TERMS

An explanation of each term used in Figure B.1-a and which might be used to calculate emission factors is shown below:

ΔT_1: This is the total length of time over which the emissions occured. If a background sample is collected, the emission time is equal to the time interval between the end of the background sample collection and the end of the emission sample collection. If no background sample is collected, the emission time is equal to the total sample enclosure time ($T_6 - T_0$).

ΔT_2: This is the flush time. It is standarized at 6 minutes.

ΔT_3: This is the purge time. This purge flow is set a t 2 ℓ/min , the 2 ℓ/min flow is begun at the end of the flush period and prior to the beginning of the collection of the emission sample. The purge flow is continued until the end of the sampling period.

ΔT_4: This is the time that it takes to fill the sample canister to the desired pressure. If the sample collection rate is known, the volume of sample can be estimated. In practice, however, pressure differentials are used to calculate the sample volume because the sample rate is not constant. However, (ΔT_4 x sample rate) is useful to check the sample volume determined by pressure differentials.

The sample volume is only important when non-evacuated sample containers are used.

Zv: This is the total volume of air passed into the sampling enclosure (Teflon bag), in cubic meters. It is equal to the flush flow rate times the flush time plus the purge flow rate times the purge time.

CT: This is the corrected VOC concentration of the sample canister. For samples collected in evacuated stainless steel canisters or Teflon sample bags, there is no dilution. For example, the evacuated cans used by WSU in this study were pumped down to approximately 30 microns. This yields a residual dead volume of less than 0.21 ml. For samples collected in cans which have been purged with a zero gas but not evacuated, a dilution factor should be used that is equal to the absolute pressure gain of the cans. The dilution factor $\frac{Pc+Pb}{Pca}$ times the TNMOC of the can (C_{ss}, C_{sb}, C_{sa} and C_{se} in Figure B.1-a) is equal to the corrected TNMOC for each sample.

Subscripts e, a, b and s designate enclosure blank, ambient air, background and emission rate samples respectively. Therefore, CT_s is equal to the concentration of the emission rate sample in $\mu g/m^3$.

The contribution of the various components which can be included in the emission sample can be calculated as shown below:

MGa: This component is the small contribution to the emission sample of the residual ambient air in the enclosure. If a background sample is collected, it will include MGa. When the bag is placed over a branch and collapsed, some residual dead volume (Ve) will remain. The ambient air in this residual volume is assumed to have a VOC burden similar to ambient air collected in the proximity of the vegetation chamber at the time of enclosure. Therefore, the dead volume of the bag is estimated and then multiplied times the corrected VOC for the ambient air sample, or MGa = (CTa) (Ve). This gives the amount of VOC contributed to the emission sample due to ambient air.

MGe: This component is the contribution from the enclosure walls to the emission sample. In some cases the enclosure may be difficult to clean, or after many consecutive sampling times it may have accumulated pitch or other emission residues. If this is suspected, a bag blank should be collected to determine the enclosure emission rate. This sample is collected in the same manner as a branch sample. The formula used to calculate the "emission rate of the chamber walls" is identical to the emission rate formula. Primes indicate that the variables apply to the "blank" sample. Ambient air can also be an additive component to the blank total for rigid enclosures. The ambient air contribution to rigid enclosures is equal to MGa (Ve'). The dead volume (Ve') of Teflon bag enclosures when collapsed during collection of the enclosure blank equals zero, hence the ambient air contribution to a Teflon bag blank is zero. The enclosure emission rate ($\mu g/m^3$) is then multiplied times the emission sample enclosure time to give an estimate of the amount of VOC "bled" from the enclosure wall (μg) during the vegetation emission period. The equation is written as:

$$MGe = \frac{CTe\ (Ve' + Zv') - CTa\ (Ve')\ \Delta T_1}{\Delta T_1'}$$

Ve', Zv' and $\Delta T_1'$ represent the dead volume, the purge plus flush volume and the length of enclosure time respectively, for a blank sample. MGe here is equal to the TNMOC concentration of the bag sample ($\mu g/m^3$) x the volume enclosed by the bag (Ve' + Zv') minus the contribution of ambient air CTa (Ve') divided by the enclosure time ΔT_1. For Teflon bag enclosures enclosures, Ve' = 0 since the bag can be completely collapsed when a blank is collected. For Teflon bag enclosure the equation therefore becomes:

$$MGe = \frac{CTe\ (Zv')}{\Delta T_1'}\ \Delta T_1$$

If $\Delta T_1 = \Delta T_1'$ (if the vegetation enclosure time is equal to the bag blank enclosure time), which is often the case, the equation is simply:

$$MGe = CTe\ (Zv')$$

If proper care is taken to clean enclosure chambers by purging and heating slightly (they can be propped open and left in the sun), MGe becomes very small. When a background sample is collected, ΔT_1 is shorter and MGe is even smaller and can therefore usually be omitted.

MGb: This is equal to the contribution from ambient air, from the vegetation enclosure and from the vegetation enclosed until ΔT_1, as determined from a "background" sample. The background sample is collected after a branch is enclosed but before any air has been added to the enclosure, and is therefore equal to the VOC concentration in the dead volume (Ve). For Teflon bag enclosures this is the time at which the bag is collapsed around the vegetation. MGb is therefore equal to the VOC of the background sample CTb times the dead volume of the bag (Ve). The dead volume is estimated using the dimension measured at the time the background sample is collected. The dead volume can also be calculated if the concentration of a relatively inert tracer such as acetylene or a halocarbon in the background sample is ratioed to its concentration in the emission rate sample using the following formula:

$$Ve = \frac{Zv}{(C_{sb}/C_{ss})-1}$$

Where C_{sb} and C_{ss} are the concentrations of the tracer in the background sample and emission rate sample respectively.

ER: This is the resulting emission factor for the vegetation. It is equal to the VOC contribution from the emission sample (CT_S) (Zv+Ve) minus the VOC contribution of the background (MGb) minus the VOC of the bag blank, divided by the chosen biomass components of the branch and the length of emission time (Sa)(ΔT_1). It is also equal to the VOC contribution of the emission sample minus the contribution of ambient air and minus the contribution from the enclosure walls.

B.1.2. EMISSION RATE FORMULAS

The emission rate formula when a background sample is collected is:

$$ER\ (\mu g/Sa \cdot min) = \frac{CTS\ (Ve + Zv) - MGb - MGe}{(Sa)\ (\Delta T_1)} \quad \text{where } \Delta T_1 = T_6 - T_1 \quad (1)$$

The emission rate formula when no background sample is collected is:

$$ER = \frac{CTS\ (Ve + Zv) - MGa - MGe}{(Sa)\ (\Delta T_1)} \quad \text{where } \Delta T_1 = T_6 - T_0 \quad (2)$$

If a background sample is collected, evacuated canisters or Teflon sample bags are used and the bag blank MGe is small, the equation is reduced to:

$$ER = \frac{Css\ (Ve + Zv) - Csb\ Ve}{(Sa)\ (\Delta T_1)} \quad (3)$$

where:

C_{ss}: equals the TNMOC measured for the emission sample ($\mu g/m^3$)

C_{sb}: equals the TNMOC measured for the background sample ($\mu g/m^3$)

Ve: equals the dead volume of the bag when collapsed around the branch (m^3)

Zv: equals the total volume of zero air put into the enclosure (m^3)

Sa: equals the chosen biomass components of the sample (g) or leaf litter or water surface area (m^2)

ΔT_1: equals the total emmission time (min) = $T_6 - T_1$.